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School of Chemical Technology
Degree Programme of Chemical Technology

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SUSTAINABILITY ASPECTS OF CRUDE SULFATE SOAP ACIDULATION TO CRUDE TALL OIL WITHIN THE EU BIOFUEL POLICY FRAMEWORK

Master's thesis for the degree of Master of Science in Technology submitted for inspection in Espoo, June 18, 2015.

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Abstract of master's thesis

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Title of thesis Sustainability aspects of crude sulfate soap acidulation to crude tall oil within the EU biofuel policy framework

Department Department of Biotechnology and Chemical Technology

Professorship Plant design **Code of professorship** KEM-107

Thesis supervisor Ville Alopaeus

Thesis advisor(s) / Thesis examiner(s) Maiju Helin, Sarwar Golam

Date 18.06.2015 **Number of pages** 83 **Language** English

Abstract

The EU biofuel policy is based on two directives, the Renewable Energy Directive and the Fuel Quality Directive. These directives set sustainability criteria for biofuels and present the general rules for calculating the greenhouse gas emissions of a fuel. However, the directives have been interpreted differently in different member states, especially concerning waste and residue feedstocks. In Finland, the greenhouse gas emissions of acidulation are currently not reported in the lifecycle emissions of a biofuel based on crude tall oil (CTO), as CTO is considered a residue of pulp production. However, the residue status of CTO has been questioned, due to its alleged intentional manufacturing in the acidulation process. This thesis aims, first, to create and implement a method for calculating the greenhouse gas emissions of typical acidulation processes in line with EU policy, and second, to determine if acidulation emissions can be separated from the pulp production emissions in a kraft pulp mill. Based on the results, the work provides recommendations for the classification of CTO under EU biofuel legislation.

Crude tall oil is generated when acid is added to a separated soap phase formed in pulp cooking. This soap has to be removed from the process and by means of acidulation, sulfur and sodium cooking chemicals in the soap can be recycled back to the pulping process. Acidulation is interlinked with the pulp mill chemical recovery cycle and constitutes a major intake of sulfur to the cycle. As the material streams from acidulation have effects also outside the acidulation process, emissions of acidulation were in this work calculated by considering the chemical balance of the whole pulp mill. Models for a typical pulp mill and three common acidulation processes were created based on literature and UPM-internal data. The emissions of the three most common acidulation processes were calculated and the sensitivity of these emissions was studied against the most important variables of both acidulation and chemical balance of the pulp mill.

It was first observed that depending on the sulfur balance of the pulp mill and acidulation inputs, an interlinked acidulation process could either increase or decrease the total emissions of the mill. Second, it was seen that the emissions of an acidulation process are more sensitive to changes in the pulp mill sulfur balance than they are to changes in the acidulation process. Thus, due to large variations in the sulfur balances between different pulp mills, or even at the same mill at different times, the emissions of acidulation cannot be reliably determined and separated from the emissions of pulp production. Moreover, the sulfur balance, which affects the acidulation emissions the most, is optimized for pulp production, not for CTO production. This supports the conclusion that acidulation emissions should be allocated to pulp, rather than to CTO.

Acidulation is an essential part of the pulp mill and an optimized way to dispose the soap. As the soap is clearly a residual stream and emissions of acidulation cannot be separated from the emissions of pulp production, no emissions can be allocated to CTO. Therefore, it is recommended that CTO is regarded as a residue in the EU biofuel legislation.

Keywords Sustainability, crude tall oil, acidulation, emission calculation, biofuels

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Diplomityön tiivistelmä

Tekijä Maria Puustinen

Työn nimi Kestävyysnäkökulmia suovan palstoitukseen mäntyöljyksi EU:n biopolttoainepolitiikan viitekehyksessä

Laitos Biotekniikan ja kemian tekniikan laitos

Professuuri Tehdassuunnittelu **Professuurikoodi** KEM-107

Työn valvoja Ville Alopaeus

Työn ohjaaja(t)/Työn tarkastaja(t) Maiju Helin, Sarwar Golam

Päivämäärä 18.06.2015 **Sivumäärä** 83 **Kieli** Englanti

Tiivistelmä

EU:n biopolttoainepolitiikka perustuu kahteen direktiiviin, uusituvan energian direktiiviin ja polttoaineiden laatudirektiiviin. Nämä direktiivit asettavat biopolttoaineille kestävyyskriteerit ja esittelevät pääperiaatteet biopolttoaineiden elinkaaren kasvihuonekaasupäästölaskennalle. Näitä direktiivejä on kuitenkin tulkittu eri jäsenmaissa eri tavoin, erityisesti koskien jäte- ja tähderaaka-aineiden määrittelyjä. Palstoituksen kasvihuonekaasupäästöjä ei tällä hetkellä Suomessa huomioida mäntyöljystä valmistetun biopolttoaineen elinkaaren päästölaskennassa, sillä raakamäntyöljy luokitellaan selluntuotannon tähteeksi. Mäntyöljyn tähdestatus on kuitenkin kyseenalaistettu viitaten sen tarkoitukselliseen tuottamiseen palstoitusprosessissa. Tämän diplomityön tavoitteina on luoda metodi palstoituksen päästöjen laskemiseksi, soveltaa sitä tyypillisille palstoitusprosesseille ja määrittää, voidaanko palstoituksen päästöt erottaa sellun tuotannon päästöistä. Tämän perusteella diplomityössä annetaan suosituksia mäntyöljyn luokittelemiseen EU:n biopolttoainelainsäädännössä.

Raakamäntyöljy syntyy, kun sellunkeitossa muodostuneeseen suopaan lisätään palstoituksessa happoa. Suopa on poistettava selluprosessista ja palstoituksen avulla suovan sisältämät sellunkeittokemikaalit, rikki ja natrium, voidaan palauttaa selluprosessiin. Palstoitus on integroitu sellutehtaan kemikaalikiertoon ja tuo siihen merkittäviä määriä rikkiä. Koska palstoituksen materiaalivirrat eivät rajaudu palstoitusprosessin sisälle, tässä työssä palstoituksen päästöt on laskettu huomioiden koko sellutehtaan kemikaalitase. Laskentaa varten työssä määritetään mallit tyypilliselle sellutehtaalle, sekä siihen integroiduille kolmelle yleiselle palstoitusprosessityypille. Työssä lasketaan näiden kolmen palstoitusprosessin päästöt ja tutkitaan herkkyysanalyysillä sekä sellutehtaan kemikaalitaseen että palstoituksen merkittävimpien muuttujien vaikutusta näihin päästöihin.

Tulosten perusteella sellutehtaan kemikaalikiertoon integroitu palstoitusprosessi voi tehtaan rikkitaseesta ja palstoituksen syötteistä riippuen joko lisätä tai vähentää sellutehtaan kokonaispäästöjä. Toiseksi, työssä havaitaan palstoitusprosessin päästöjen olevan herkempiä sellutehtaan rikkitaseen muutoksille, kuin muutoksille itse palstoitusprosessissa. Koska rikkitaseet eri sellutehtailla, tai jopa samalla tehtaalla eri aikoina ovat hyvin erilaisia, ei palstoituksen päästöjä voida luotettavasti määrittää ja erottaa selluntuotannon päästöistä. Lisäksi, sellutehtaan rikkitasetta optimoidaan sellun tuotannon ehdoilla, ei raakamäntyöljyn tuotannon ehdoilla. Näistä syistä palstoituksen päästöt tulisi kohdentaa raakamäntyöljyn sijaan sellulle.

Palstoitus on tärkeä osa sellutehtaan kemikaalikiertoa ja optimoitu tapa hävittää prosessista erotettava suopa. Koska suopa on selkeästi tähdevirta, eikä palstoituksen kasvihuonekaasupäästöjä voida erottaa sellun tuotannon päästöistä, ei raakamäntyöljylle voida kohdentaa päästöjä. Täten suositus on, että raakamäntyöljy tulisi EU:n biopolttoainelainsäädännössä tulkita sellun tuotannon tähteeksi.

Avainsanat Kestävyys, mäntyöljy, palstoitus, päästölaskenta, biopolttoaineet

Preface

This work was conducted at UPM Biofuels during spring 2015 while the first commercial batches of crude tall oil based renewable diesel were produced. I am happy that in addition to writing my thesis, I was able to participate in the start-up phase of the first UPM Biorefinery.

I would like to thank Maiju Helin, my manager and instructor at UPM Biofuels for all the advice and guidance, and especially for showing confidence in me from the very beginning. I would also like to thank Sarwar Golam, my instructor from Aalto University, for valuable comments and encouragement during this project. Likewise, I thank Professor Jukka Koskinen, who supervised my thesis work in practice. Furthermore, I owe to Sami Saarela, Aleksi Nurmi, Ismo Tapalinen, Marko Sundqvist, Markku Kauppinen, Esa Hassinen, Andreas Rönnqvist and Matti Tikka from UPM, for sharing their knowledge and arranging the time to discuss about my thesis subject with me.

In addition, I want to thank all my colleagues at UPM for taking me a part of the team. You made my workdays enjoyable and I could not have imagined a better environment to learn new things. Finally, I would like to thank J-P for peer support.

Thank You!

June 18, 2015, Espoo

Maria Puustinen

Contents

1 Introduction

In order to mitigate global warming, the European Union has set targets to decrease greenhouse gas emissions and to increase the use of renewable energy in its member states. By the year 2020, 10% of transport fuels used in EU shall be renewable. The biofuels counted towards the target have to fulfill a certain sustainability criteria, one of which being a minimum greenhouse gas emissions saving in comparison to fossil fuel. [1] The general principles for calculating the lifecycle greenhouse gas emissions of a fuel, are presented in EU directives, but are in many ways open to interpretation.

Depending on the feedstock, different emission calculation rules are applied. One particularly debatable matter relates to defining waste and residue feedstocks. Current EU directives do not define wastes or residues, but state, that for the calculation of lifecycle greenhouse gas emissions of biofuels produced from wastes or residues, no up-stream emissions before the generation of the residue have to be taken into account [1]. This means, that the process where the waste or residue is generated is left outside the system boundary of calculation and the emissions of a waste or residue are set to zero. A simplified principle of the lifecycle emission calculation is presented in Figure 1. The process emissions are defined by the emissions from production of the energy and material inputs used inside the system boundary, direct emissions generated and emissions created in handling of the waste streams. These emissions are calculated based on the quantities of inputs used and wastes created, which are converted to emissions using input and waste specific emissions factors. As the emissions of waste and residue streams are considered zero, all emissions are then allocated to the product or products of the process.

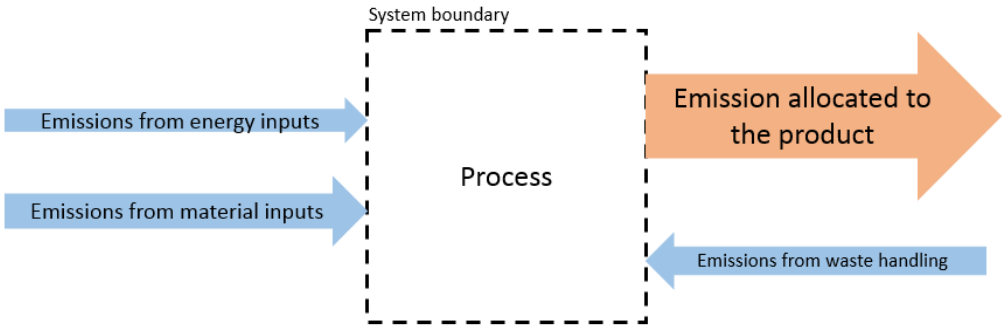

Figure 1. The basic principle for greenhouse gas emission calculation. All emissions from inputs and waste handling are allocated to the product. No emissions are allocated to waste or residue streams.

UPM has recently started a biorefinery in Lappeenranta, which produces renewable diesel fuel from crude tall oil (CTO). Crude tall oil, named by the Swedish word for pine oil "tallolja", is a dark viscous liquid obtained as a side-stream from sulfate pulping process, also called kraft pulping. The formation of CTO originates in softwood cooking, where fatty and resin acids of the wood are saponified by the alkaline liquor. Neutral wood extractives, such as sterols, dissolve in the soap phase formed. This crude sulfate soap (CSS) has to be removed from the pulping process and is most commonly converted to crude tall oil by an acidulation process, which is interlinked within the pulp mill.

The definition of CTO has caused a debate within the EU. Currently, authorities of each EU member state have been able to decide whether they define CTO as a product or a residue. Currently, Finland and Sweden define CTO as a processing residue, but this classification has been questioned arguing that CTO is intentionally extracted and manufactured from CSS using specific acidulation process technologies [2, 3]. CTO is also listed as a processing residue in the final draft of a directive amending the current EU biofuel legislation, expected to be adopted later this year. However, currently EU member states can interpret residues differently, which has led to varying emission calculation methodologies and reporting requirements across Europe, producing market restrictions.

1.1 Aim of the work

The residue status of CTO has been questioned due to the alleged intentional manufacturing of CTO in the acidulation process. Therefore, it is important to understand the effect of acidulation process to the total greenhouse gas emissions of a CTO based biofuel, although in Finland these emissions do not currently need to be reported. In this work, the emissions of typical acidulation processes are studied with regards to EU legislation. As the acidulation process is normally integrated with the kraft pulping process, this work focuses on the separation of acidulation-induced emissions from the pulp production caused emissions in the pulp mill.

The purpose of the work is to:

1) Create and implement a method for calculating the greenhouse gas emissions of CSS acidulation to CTO in selected typical kraft pulp mill integrated processes. The method shall be in line with EU biofuel policies.
2) Determine if acidulation emissions can be separated from the pulp production emissions in a kraft mill and
3) Provide recommendations on how CTO should be classified in EU biofuel legislation.

1.2 Structure of the work

The literature part consists of three chapters. Chapter 2 presents the policy framework and resulting authority requirements for the biofuel lifecycle emission calculations in EU. Chapter 3 provides an overview of the main types of acidulation processes. The effects of acidulation processes on the material and energy balances of the pulp mill are studied in chapter 4. The purpose of the evaluation is to determine, if possible indirect emissions created elsewhere in the pulp mill due to acidulation should be considered in the calculations.

In the applied part, definitions for the system boundaries for emissions calculation are presented, according to the information collected. Corresponding methods for emission calculation are applied for the most common acidulation process types integrated with a kraft mill, and the generalizability of the results is estimated in a sensitivity analysis. Finally, the residue status of CTO is discussed in the light of the findings and conclusions are drawn.

LITERATURE PART

2 EU biofuel policy framework

The European Union has recognized increasing the use of biofuels and bioliquids as one of the main ways to mitigate climate change. Biofuels are defined as liquid or gaseous fuels produced from biomass and used for transport. Bioliquids, on the other hand, are liquid fuels used for energy purposes other than transport. As production of biofuels is still economically uncompetitive with fossil fuels, the biofuel market is dependent on legal obligations and financial support, such as tax reliefs or investment aid. In EU, the main policies enhancing the use of biofuels are set in the Renewable Energy Directive (RED) [1] and the Fuel Quality Directive (FQD) [4], which are presented in section 2.1. In these directives, obligations to increase the use of biofuels are set for each member state, as well as sustainability criteria for the biofuels to be counted towards these targets.

However, as the legal acts of EU are set as directives, they are non-specific in the means of fulfilling these requirements and each member state has been obligated to adopt the contents of the directives into their own national regulations. This has made different interpretations of the directive possible and led to variations in the laws of different member states. In Finland, the directives were adopted to national laws by the Act on Biofuels and Bioliquids in 2013 [5] and in the amendment of the Distribution Obligation Act in 2010 [6], presented in section 2.2.

Section 2.3 discusses the different interpretations of wastes and residues in EU member states. The sustainability criteria applied for a fuel are dependent on the classification of the feedstock. The compliance with the criteria is monitored through EU approved certification schemes, which are presented briefly in section 2.4. The minimum greenhouse gas emission saving criteria is equal for all biofuels, but it is calculated differently for wastes and residues. Section 2.5 outlines the rules for the calculation of greenhouse gas emissions. Finally, section 2.6 overviews the expected future changes in the EU biofuel policies.

2.1 Renewable Energy Directive and Fuel Quality Directive

The most important policies regarding biofuels are set in the EU Renewable Energy Directive (RED) 2009/28/EC [1] and the Fuel Quality Directive (FQD) 2009/30/EC [4]. Many of the main provisions considering biofuels are present in both directives. EU-wide targets for the shares of renewable energy are set in RED article 3. By the year 2020, the share of renewable energy used in EU needs to be at least 20% of the total energy consumption and 10% of the energy used in transport. RED Annex I presents individual renewable energy targets for each member state, with the target for Finland being 38 % of the total consumption of energy by 2020 [1]. FQD, on the other hand, sets environmental specifications for the fuels used in EU [4].

Both RED and FQD describe the sustainability criteria that biofuels need to fulfill in order to be counted towards renewable energy targets. In RED, the criteria are presented in article 17. If the criteria are not met, the fuel is regarded as fossil when calculating the fulfillment of the targets and obligations. Furthermore, fuels that fail to meet the criteria will not be eligible for financial support set for promoting the use of biofuels and bioliquids. The main contents of the sustainability criteria are the following: [1, 4]

I. Setting of minimum greenhouse gas emission savings:
   The greenhouse gas emission saving from the use of biofuels and bioliquids has to be at least 35% until the end of the year 2016 and from 2017 at least 50%. For new installations (production started on 2017 or after), the greenhouse gas emission saving has to be at least 60% from the year 2018.

II. Excluding biomass feedstocks obtained from land with high biodiversity:
   Raw material obtained from primary forest, from areas designated for nature protection purposes or from highly biodiverse grassland cannot be used for production of biofuels or bioliquids.

III. Excluding biomass feedstocks obtained from land with high carbon stock:
Raw material obtained from high carbon stock land, such as wetlands or forests, cannot be used for production of biofuels or bioliquids unless the land use status is not changed after January 2008.

IV. Excluding biomass feedstocks obtained from dried peatland:
Raw material obtained from land that was peatland in January 2008 cannot be used for the production of biofuels or bioliquids unless evidence is provided that the cultivation and harvesting of that raw material does not involve drainage of previously undrained soil.

RED states that if a biofuel or bioliquid fulfills these criteria, member states should require no other sustainability criteria to be met for taking the bioliquid or biofuel into account in their renewable energy share calculations. Biofuels and bioliquids only need to accomplish the minimum greenhouse gas saving if produced from waste and residues, other than agricultural, aquaculture, fisheries and forestry residues. For these biofuels sustainability criteria II-IV are not considered. [1] However, neither RED nor FQD does specify the means to define wastes and residues. Specifications for calculating the greenhouse gas saving of a biofuel or bioliquid are provided in both directives and presented in more detail in section 2.5. [1, 4]

In addition to renewable energy targets and sustainability criteria for biofuels and bioliquids, RED tries to mitigate climate change by presenting a concept for promoting the use of advanced biofuels. The so-called double counting rule presented in article 21 means that biofuels made from wastes, residues, non-food cellulosic material, and ligno-cellulosic material are counted towards the targets twice their energy content. [1] Thus, a fuel supplier can fulfill a 20% biofuel distribution obligation by mixing only 10% of advanced biofuels with a fossil fuel. Therefore, in theory, the value of an advanced biofuel is enhanced by the price difference between fossil and traditional biofuel when compared to other biofuels. Although RED presents double counting as mandatory, it has not been adopted for use in all EU member states. Moreover, different interpretations of the term residue result to varying double counting rules in different countries.

2.2 National legislation in Finland

Finnish biofuel policy is based on Act on Biofuels and Bioliquids 393/2013 [5] and the Distribution Obligation Act 446/2007 [6] which implement the policies of RED and FQD with additional national targets and methods for assuring the sustainability of biofuels in Finland. Act on Biofuels and Bioliquids adopts the sustainability criteria of RED and FQD to Finnish legislation and describes how the compliance of the criteria shall be proved. In Finnish legislation, a fifth sustainability criterion is added to the four criteria presented in RED. The fifth criterion extends the conditions of EU agricultural subsidies, regarding good practices and environmental performance, to apply also to cultivation of biofuel feedstocks.

The Distribution Obligation Act sets a national target for gradually increasing the share of renewable energy used in transport to 20% by the year 2020. This is done by obligating the fuel distributors to supply biofuels to consumption in increasing shares. The obligated shares are 8% of the total supplied energy content for the year 2015, 10% for 2016, 12% for 2017, 15% for 2018, 18% 2019 and 20% for 2020 and after. The biofuels supplied must fulfill the sustainability criteria adopted in Act on Biofuels and Bioliquids. Double counting is used for advanced biofuels made from waste, residue, non-food cellulosic and ligno-cellulosic raw materials as set in RED. [6]

2.3 Interpretations of wastes and residues in EU member states

According to RED, the use of wastes and residues as a biofuel feedstock is promoted in three ways. First, the greenhouse gas calculation is eased for wastes and residues, as no emissions are allocated to them before the waste or residue is generated. Second, the traceability requirements for wastes and residues, other than agricultural, aquaculture, fisheries and forestry residues are reduced, as the sustainability criteria II-IV regarding the origin of the feedstock are not considered. Third, biofuels produced from wastes and residues should be double countable. [1] Yet, this is not the case in all member states.

EU directives do not currently provide definitions of wastes and residues, but in RED Annex V examples of agricultural crop residues are listed and crude glycerine is given as an example of a processing residue [1]. The first official EU document defining waste and residue in the biofuel context is Communication from the Commission (2010/C 160/02) which clarifies the possible practical implementation of the EU directives regarding biofuels. EU Communications have no binding character but member states *can* implement them in practice. [7]

The communication defines waste as *any substance or object which the holder discards or intends or is required to discard. Raw materials that have been intentionally modified to count as waste (e.g. by adding waste material to a material that was not waste) should not be considered as qualifying*. In the communication, residues are listed to include agricultural, aquaculture, fisheries and forestry residues, and processing residues. Processing residue is defined as *a substance that is not the end product(s) that a production process directly seeks to produce. It is not a primary aim of the production process and the process has not been deliberately modified to produce it*. Crude glycerine, already mentioned in RED, tall oil pitch, and manure are listed as examples of residues. [7]

The decision on whether a certain feedstock is classified as waste or residue is in practice made by the national authorities in each member state. In Finland, definitions of waste and residue are included to both Act on Biofuels and Bioliquids and Distribution Obligation Act and are in line with the definitions provided in the communication. [5, 6] The Finnish legislation does not directly list any examples of substances regarded as wastes or residues. However, article 38 of Act on Biofuels and Bioliquids mandates Energy Authority to monitor the compliance of the legislation and, by petition, to provide advance information on whether a specified substance will be considered waste, residue, non-food cellulosic or ligno-cellulosic raw material and therefore be eligible for double counting. The advance information is valid until further notice, and can be canceled by resolution of judicial authority on the change of interpretation of provision or other particular

reason. [5] Currently, Energy Authority has considered crude tall oil, used as biofuel feedstock by UPM, as a residue [8].

Wastes and residues are interpreted differently in different countries leading to situation, where certain residue and waste based biofuels only have a market in countries that have the same residue or waste classification for the raw material. Although a biofuel supplier would provide an international certificate of compliance with the sustainability criteria for a biofuel, it will not have market in countries, where the local legislation does not approve it to be calculated towards the renewable energy mandate of this country. Classification to waste or residue does neither always mean that the material is double countable. Some countries, including Spain and Sweden have never adopted the double counting principle presented as obligatory in RED and Germany has abolished double counting in the beginning of the year 2015 [9].

Member states have also presented additional criteria for biofuels counted towards their renewable energy targets, despite that this is straightforwardly prohibited in RED. For example, in Belgium and Spain, only selected producers can supply biofuels towards their biofuel mandate, and Germany has banned all fuels from animal fat feedstocks for even single counting towards their mandate. [10] Yet, the European Commission has verified the full transposition of the EU directives to the national laws of these member states [11].

Examples of different interpretations of waste and residue materials, as well as double counting, are compiled to Table 1. The table includes the current interpretations in selected member states as well as the wastes and residues listed in EU documents. While RED [1] is currently the only effective legislation listing examples of wastes and residue, many member states have decided to follow the listing provided in Communication from the Commission (CC) [7]. For comparison, the table also includes the final draft version of ILUC directive [12], although it has not yet been officially adopted. The ILUC directive is discussed in more detail in section 2.6.

Table 1. Wastes, residues and double counting in EU legislation and some member states according to public information. ILUC directive is included according to European Parliament second reading proposal.

Double counting in use Double counting NOT in use Listed as waste or residue **Feedstock**	Waste or residue according to RED	Waste or residue according to CC	Waste or residue according to ILUC	Finland	France	Germany	Italy	The Netherlands	Spain	Sweden	United Kingdom
Animal fat /tallow category 1			■	■	■		■	■	■	■	■
Animal fat /tallow category 2			■	■	■		■	■	■		
Animal fat /tallow category 3				■							
Bagasse	■		■			■		■			■
Bark			■			■		■		■	
Biomass fraction of industrial waste not fit for use in the food or feed chain			■	■		■					
Branches, tree tops (forest residue)			■					■		■	
Brown grease /grease trap fat						■				■	■
Brown liquor, black liquor			■							■	■
Cashew nut shell liquid (CSNL)								■			■
Corn /maize cobs	■		■					■		■	■
Crude glycerine	■	■	■			■	■	■		■	■
Crude tall oil (CTO)			■	■			*			■	
Empty Palm Fruit Bunches (EFB)			■					■			
Fiber sludge			■								
Food waste				■		■		■		■	■
Grape marc			■		■		■	■		■	■
Husks	■		■			■		■		■	■
Leaves and needles from forest industry			■								
Lignin			■								■
Manure		■	■			■		■		■	■
Methanol from pulp processing				■							
Nut shells	■		■					■		■	■
Organic municipal solid waste (MSW)			■	■				■		■	■

Feedstock	Waste or residue according to RED	Waste or residue according to CC	Waste or residue according to ILUC	Finland	France	Germany	Italy	The Netherlands	Spain	Sweden	United Kingdom
Palm oil fatty acid distillate (PFAD)				■							
Palm oil mill effluent (POME)			■			■		■			■
Palm oil separated from silicate precipitate or waste water sludge				■							
Palm oil stearine				■							
Palm sludge oil from POME						■					■
Pre-commercial thinnings from forest industry			■								
Rapeseed residue						■					■
Refinery fatty acids, residual acid oils, distillation residues				■		■	■			■	**
Renewable component of end-of-life-tyres											■
Sawdust and cutter chips			■	■				***		■	■
Sewage sludge			■	■				■		■	
Slaughterhouse waste										■	
Soapstock acid oil						■				■	****
Spent bleaching earth								■			■
Starch slurry (low grade)						■					■
Straw	■	■	■			■		■		■	■
Sugar beet residues						■		■		■	■
Tall oil pitch		■	■	■		■		■		■	■
Technical corn oil (TCO)				■		*****					
Turpentine from pulp processing or tall oil processing				■							
Used cooking oil (UCO) entirely of vegetable origin			■		■	■	■	■	■	■	■
Used cooking oil (UCO) entirely or partly of animal origin			■		■		■	■	■	■	■
Waste pressings from production of vegetable oils											■
Wine lees			■		■	■	■			■	■
References	[1]	[7]	[12]	[8]	[10,13]	[14]	[10]	[15]	[10]	[16]	[17]

Double counting in use
Double counting NOT in use
Listed as waste or residue

*** classified as advanced feedstock, but not eligible for double counting**

**** if original fatty acids are residues**

***** with exceptions**

****** when contaminated with sulfur**

******* of genetically modified corn**

Positions towards CTO are varying. Currently, the decision-making authorities have classified CTO as a residue only in Finland and Sweden. Sweden has not adopted the double counting principle, making CTO double countable only in Finland. Italy has classified CTO as an advanced biofuel, but not included it on the double counting list. United Kingdom and The Netherlands have explicitly banned CTO from double counting. In the Netherlands, this is due to interpretation that the double counting rules of RED are not applicable for feedstocks that already have existing non-bioenergy uses. However, tall oil pitch (TOP), listed as a residue in the Commission Communication, is double countable in the Netherlands although, in addition to CTO, also TOP has existing uses in the chemical industry [18].

In summary, the national regulations in EU member states vary from slightly different interpretations on the definitions of waste and residue to direct violations of the EU directives, as RED and FQD have not been adopted as such. In addition, the changes of the policies have been unpredictable, which together with the inconsistency of the interpretations make the business environment challenging for a biofuel supplier.

2.4 Certification schemes

According to RED article 18, both national or international voluntary schemes and agreements can be used to measure greenhouse gas emissions savings and prove the compliance with the sustainability criteria [1]. Communication from the Commission 2010/C 160/01 further clarifies this statement. According to the communication, the compliance with sustainability criteria can be proved through an international voluntary scheme, national scheme of an EU member state, or through bilateral and multilateral agreements between EU and third countries. [19]

RED article 18 presents guidelines for a mass balance system, which has to be used by economic operators to show compliance with the sustainability criteria. The main requirement for the system is that incoming material to a mixture should have the same quantity and sustainability characteristics than outgoing material from the mixture. The mass balance system has to be designed so, that all sustainability characteristics of a

mixture of raw material or biofuel can be assigned to the corresponding fractions of the mixture at all times. [1] The sustainability characteristics in this context mean the compliance of sustainability criteria set in RED. As the first requirement is accomplishing the minimum greenhouse gas saving, the lifecycle emissions of the biofuel have to be monitored within the mass balance system. Member states are obligated to designate biofuel suppliers to monitor and report biofuel lifecycle greenhouse gas emissions by the Fuel Quality Directive. [4]

EU Commission currently approves 19 different voluntary certification schemes [[20]. Different schemes might have slight differences in the detailed calculation methods or definitions of emissions factors, but all are based on the calculation rules presented in Renewable Energy Directive. The calculation rules of RED, and more detailed instructions for process emissions calculation according to Finnish national scheme and International Sustainability and Carbon Certification (ISCC) are presented in the next chapter.

2.5 Calculation of the lifecycle greenhouse gas emissions of biofuels

The lifecycle greenhouse gas emissions are calculated following the basic principles of lifecycle analysis (LCA) by taking into account emissions generated by all energy and material inputs needed and wastes created along the supply chain of the biofuel within the system boundaries set in RED. The analysis is extremely important, as despite of a renewable raw material, an energy intensive production chain may also result to a biofuel having higher greenhouse gas emissions than fossil fuel. The lifecycle greenhouse gas emissions of a biofuel are always compared to those of a fossil comparator, and according to the sustainability criteria set in RED, a minimum emission saving must be achieved.

In article 19, Renewable Energy Directive provides three options for the calculation of lifecycle greenhouse gas emissions of a biofuel. First is to use default emission values for production chains listed in the directive. Second option is to use real values calculated according to instructions provided. Third option is to use default values in combination with real calculated values. [1]

RED Annex V Part C clarifies the rules for calculating the greenhouse gas emissions of a biofuel. The gaseous emissions taken into account for the greenhouse gas emission calculation are carbon dioxide (CO_2), nitrous oxide (N_2O) and methane (CH_4). The CO_2 emissions include only fossil carbon, as the CO_2 released in the incineration of biomass is considered to have absorbed to the biomass when it is grown. Therefore, the incineration of biomass results to zero CO_2 increase when the total lifecycle greenhouse gas emissions are considered.

The emissions are calculated as grams of CO_2 equivalents per megajoule of fuel (gCO_2eq/MJ), for which the global warming potential of all greenhouse gases is transformed to that of CO_2. The factors for calculating the CO_2 equivalence are the following:

CO_2: 1 gCO_2eq/g
N_2O: 296 gCO_2eq/g
CH_4: 23 gCO_2eq/g

For renewable diesel produced from tall oil, no default values exist. Hence, real calculated values have to be used. The general equation for lifecycle greenhouse gas emission calculation is the following:

$$EM\ [gCO_2eq/MJ] = e_{ec} + e_l + e_p + e_{td} + e_u - e_{sca} - e_{ccs} - e_{ccr} - e_{ee}\ , \qquad (1)$$

where

- E is the total emissions from the use of the fuel in gCO_2eq/MJ of biofuel,
- e_{ec} is the emissions from the extraction or cultivation of raw materials in gCO_2eq/MJ of biofuel,
- e_l is the annualized emissions from carbon stock changes caused by land-use change in gCO_2eq/MJ of biofuel,
- e_p is the emissions from processing in gCO_2eq/MJ of biofuel,
- e_{td} is the emissions from transport and distribution in gCO_2eq/MJ of biofuel,
- e_u is the emissions from the fuel in use in gCO_2eq/MJ of biofuel,
- e_{sca} is the emission saving from soil carbon accumulation via improved agricultural management in gCO_2eq/MJ of biofuel,

e_{ccs} is the emission saving from carbon capture and geological storage in gCO_2eq/MJ of biofuel,

e_{ccr} is the emission saving from carbon capture and replacement in gCO_2eq/MJ of biofuel, and

e_{ee} is the emission saving from excess electricity from cogeneration in gCO_2eq/MJ of biofuel.

For biofuels and bioliquids produced from process residues, no extraction, cultivation, or annualized emissions from land use change are reported, as emissions are considered zero in the point where the residue is generated. Furthermore, no emission saving from soil carbon accumulation via improved agricultural management can be accounted for process residues. [1]

In the case of renewable diesel produced from tall oil, no carbon capture and storage or replacement is performed and no emissions can be accounted for emission saving from excess electricity from cogeneration. The emissions from the fuel in use are regarded as zero for biofuels and bioliquids, as the carbon released in the burning of the fuel is considered to have absorbed to the biomass when raw material is grown. The N_2O and CH_4 emissions of the fuel in use are also excluded from the inspection as they are presumed to be equivalent to the fossil fuel emissions from use. Therefore, for tall oil renewable diesel the equation for calculation of the lifecycle greenhouse gas emissions is reduced to the sum of processing emissions and emissions from transport and distribution:

$$EM\ [gCO_2eq/MJ] = \ e_p \ + \ e_{td}. \qquad (2)$$

Emissions from processing, e_p, include emissions created by handling of wastes and leakages and emissions from the production of chemicals or products used in processing. [1] For common substances, these can be taken into account by using emission factors from references approved by sustainability scheme certifiers. Consumption of electricity is taken into account by using average emission intensity of the production and distribution of electricity in a defined region, if electricity is not produced in the fuel production plant [1].

If several products are generated in the same process, the emissions created until that point are allocated between the products in proportion to their energy content (lower heating value, LHV). In addition to the process emissions, all previous emissions generated by the raw material are also allocated between products. Wastes and residues are regarded to have zero emissions at the point they are generated, so emissions are only divided between products and by-products. [1]

Allocation takes place directly in the point where the by-products are generated. Yet, the Renewable Energy Directive specifies, that in case fuels produced in refineries, unit of analysis for the analysis shall be the refinery. [1] RED does not specify the concept of a refinery, but for example in ISCC instructions, this is understood as interlinked processes. According to ISCC and Finnish Energy authority, no allocation should be done before a point where no energy or material feedback streams are connected to any up-stream parts of the process. [21, 22] This means setting the system boundary to cover the whole refinery, as pictured in Figure 2, and allocating emissions only for product streams exiting the system boundary, not for intermediate products.

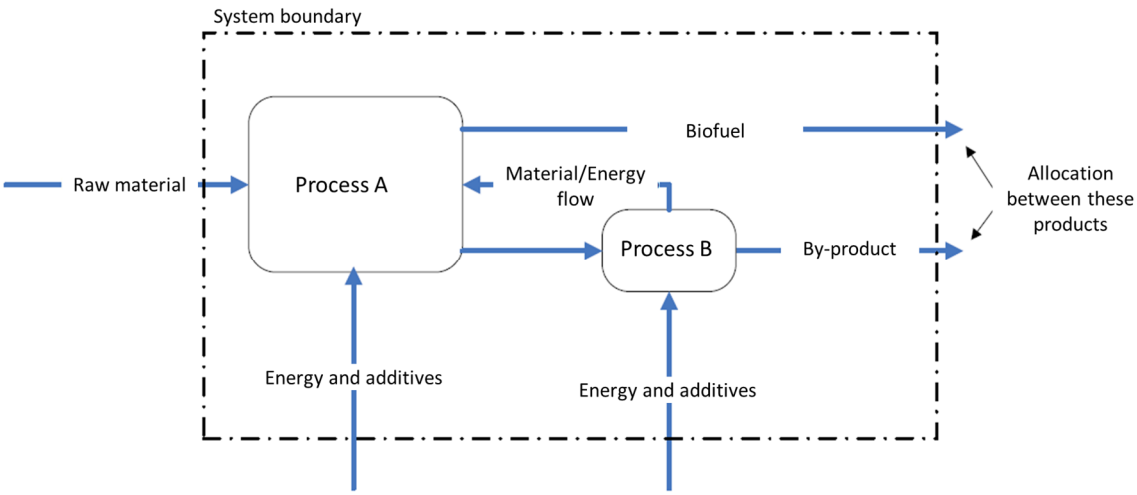

Figure 2. System boundary and allocation for a process containing interlinked process parts. Process part A and Process part B compose an interlinked process. [22]

Practical definitions of policy considering the setting of system boundaries for the calculation of processing emissions are scarce. In RED, two directions are given, one being

the exclusion of analyzing interlinked processes separately and another is excluding emissions from the manufacture of machinery and equipment from calculation [1]. Therefore, it is due to interpretation, if other indirect effects should be considered or not. Certification scheme providers might apply varying rules, for example, the Finnish Energy Authority states that indirect effects caused by the biofuel production should not be included in the calculations [22], but does not specify which emissions are considered indirect. The problems with defining the system boundary are especially significant when calculating processing emissions for acidulation of CSS to CTO.

Emissions from transport and distribution, e_{td}, consist of emissions from the transport and storage of raw and semi-finished materials and from the storage and distribution of finished materials. [1] For the calculation of transport emissions, routes and transport modes need to be known.

When the total lifecycle greenhouse gas emissions of a fuel are known, the greenhouse gas emission saving is calculated as:

$$S\,[\%] = \frac{EM_F - EM}{EM_F} * 100\ \%, \qquad (3)$$

where

S is total emission saving percentage from the use of the biofuel,

EM is total emissions from the biofuel in gCO_2eq/MJ of the biofuel, and

EM_F is total emissions from the fossil fuel comparator in gCO_2eq/MJ of the fossil fuel.

The fossil fuel comparator for renewable diesel is the average emission from fossil diesel fuel, 83.8 gCO_2eq/MJ. A newer value can be used, if such is available. [1]

When raw material logistic or processing emissions are calculated, it is often more practical to calculate emissions per kg or ton of raw material, rather than per MJ of raw material, so that the emissions can be allocated to products based on mass yields. ISCC and Finnish Energy Authority instruct that the process emissions should be calculated based on the following equations. The basis for the calculation is the previous year and

annual average figures can be used. The processing emissions created per kilogram of product are:

$$\mathrm{EM_p} = \frac{\mathrm{EM_{electricity\ consumption}}\left[\frac{\mathrm{kgCO_2}}{\mathrm{yr}}\right] + \mathrm{EM_{heat\ production}}\left[\frac{\mathrm{kgCO_2}}{\mathrm{yr}}\right] + \mathrm{EM_{inputs}}\left[\frac{\mathrm{kgCO_2}}{\mathrm{yr}}\right] + \mathrm{EM_{waste\ water}}\left[\frac{\mathrm{kgCO_2}}{\mathrm{yr}}\right]}{\mathrm{yield_{main\ product}}\left[\frac{\mathrm{kg}}{\mathrm{yr}}\right]}, \quad (4)$$

where

emission (EM) caused by the consumption of electricity is

$$\mathrm{EM_{electricity\ consumption}} = \mathrm{electricity}\ \left[\frac{\mathrm{kWh}}{\mathrm{yr}}\right] * \mathrm{EF_{regional\ electricity\ mix}}\left[\frac{\mathrm{kgCO_2}}{\mathrm{kWh}}\right], \quad (5)$$

emission caused by the production of heat for internal use is

$$\mathrm{EM_{heat\ production}} = \mathrm{fuel\ consumption}\ \left[\frac{\mathrm{kg}}{\mathrm{yr}}\right] * \mathrm{EF_{fuel}}\left[\frac{\mathrm{kgCO_2}}{\mathrm{kg}}\right], \quad (6)$$

emission caused by each input, e.g. chemical, used in processing is

$$\mathrm{EM_{inputs}} = \mathrm{inputs}\ \left[\frac{\mathrm{kg}}{\mathrm{yr}}\right] * \mathrm{EF_{additional\ inputs}}\left[\frac{\mathrm{kgCO_2}}{\mathrm{kg}}\right], \quad (7)$$

and emission caused by the treatment of waste waters from the process is

$$\mathrm{EM_{waste\ water}} = \mathrm{waste\ water}\ \left[\frac{\mathrm{l}}{\mathrm{yr}}\right] * \mathrm{EF_{waste\ water}}\left[\frac{\mathrm{kgCO_2}}{\mathrm{l}}\right]. \quad (8)$$

The emissions factors, EF, for each input and waste stream can be obtained from certain lifecycle inventory databases [23, 24] or other source accepted by the auditor of the sustainability scheme. The factors are estimates of the typical emissions generated in the lifecycle, such as in manufacturing and distribution of the input, or handling of waste, per unit of quantity of the input used or waste created. For energy inputs, the emissions

factors are regional and hence dependent on the forms of energy production in the region.

2.6 Future amendments of the EU directives

The basic rules of emissions calculations are not expected to be changed in the near future. However, amendments to the directives are pending. In April 28, 2015, the European Parliament approved a second reading position of the so-called ILUC directive [12], which amends EU biofuel policies set in RED and FQD. In this directive, the definitions of wastes and residues are finally provided, and CTO is included in the list of processing residues. The directive will still undergo legal-linguistic finalization, before it will be accepted by the European Council and adopted to EU legislation. However, this procedure is purely formal and no modifications to the contents will be made. After the adoption of the ILUC-directive, the member states will have 24 months to implement the directive in their national legislation, presumably, harmonizing the residue status of CTO in EU in the year 2017.

The abbreviation ILUC in the name of the directive refers to indirect land use change. The directive was first meant to tackle the problem of cultivated biofuel feedstocks causing high indirect emission effects by expansion of croplands. However, the current ILUC directive still does not require the ILUC emissions to be calculated towards to total greenhouse gas emissions of a biofuel and thereby does not exclude non-emissions-saving traditional biofuels to be counted towards the renewable energy targets. [12]

From the point of view of CTO utilization, the most important content of the ILUC directive is that CTO is added in the Annex IX part A list of double countable feedstocks. The list includes among others *biomass fraction of wastes and residues from forestry and forest-based industries, i.e. bark, branches, pre-commercial thinnings, leaves, needles, tree tops, saw dust, cutter shavings, black liquor, brown liquor, fibre sludge, lignin and tall oil.* In addition, definitions of waste and residue are added to the new directive, in line with the definitions provided in the EU communication, presented in section 2.3. After the implementation of ILUC, biofuels made of CTO will also be counted towards a target set

for advanced biofuels. Each member state is obligated to set their own target, for which a reference target of 0.5% of all energy used in transport is proposed. However, the target can also be lower. [12]

The finalization of the ILUC directive has not ended the debate considering the residue status of CTO. As concluded before, previous EU directives have not been implemented in all member states as such, and the future will tell how individual member states decide to interpret and implement the ILUC directive. However, the interpretations on wastes and residues should be at least partly harmonized in the following years.

3 Crude tall oil recovery in a kraft pulp mill

As the acidulation process, where CTO is generated, is often used as an argument against the residue interpretation, the emission effects of the acidulation process are studied in this work. In this chapter, acidulation is described as a part of the kraft pulp mill chemical recovery cycle, and three most common acidulation process types, concerning inputs and outputs, are presented. As machinery is excluded from the processing emission calculations by RED [1], the analysis of the processes is based purely on material and energy balances, and the technology is not of interest.

Crude tall oil is produced by acidulation of crude sulfate soap, which is a side-stream generated in the kraft pulping process. Kraft pulping, also known as sulfate pulping, is the most commonly used pulp production method in the world. Acidulation process is typically integrated with the kraft pulp mill, as seen in Figure 3. Hence, the setting of the system boundary for process emission calculation is not straightforward. Acidulation is interlinked with the pulp mill chemical recovery cycle (pictured in green in Figure 3) and possibly also with bleaching chemical manufacturing. Inside the chemical cycle, the needed additions of sulfur and sodium containing chemicals are dependent on the sulfur and sodium balances of the mill, which are affected by acidulation. The acidulation process increases both sulfur and water amount of the chemical recovery cycle. Hence, acidulation may cause a need for sulfur removal elsewhere in the pulp mill and increase the energy need of the evaporation plant. The effects of acidulation on the chemical balances are studied in more detail in chapter 4.

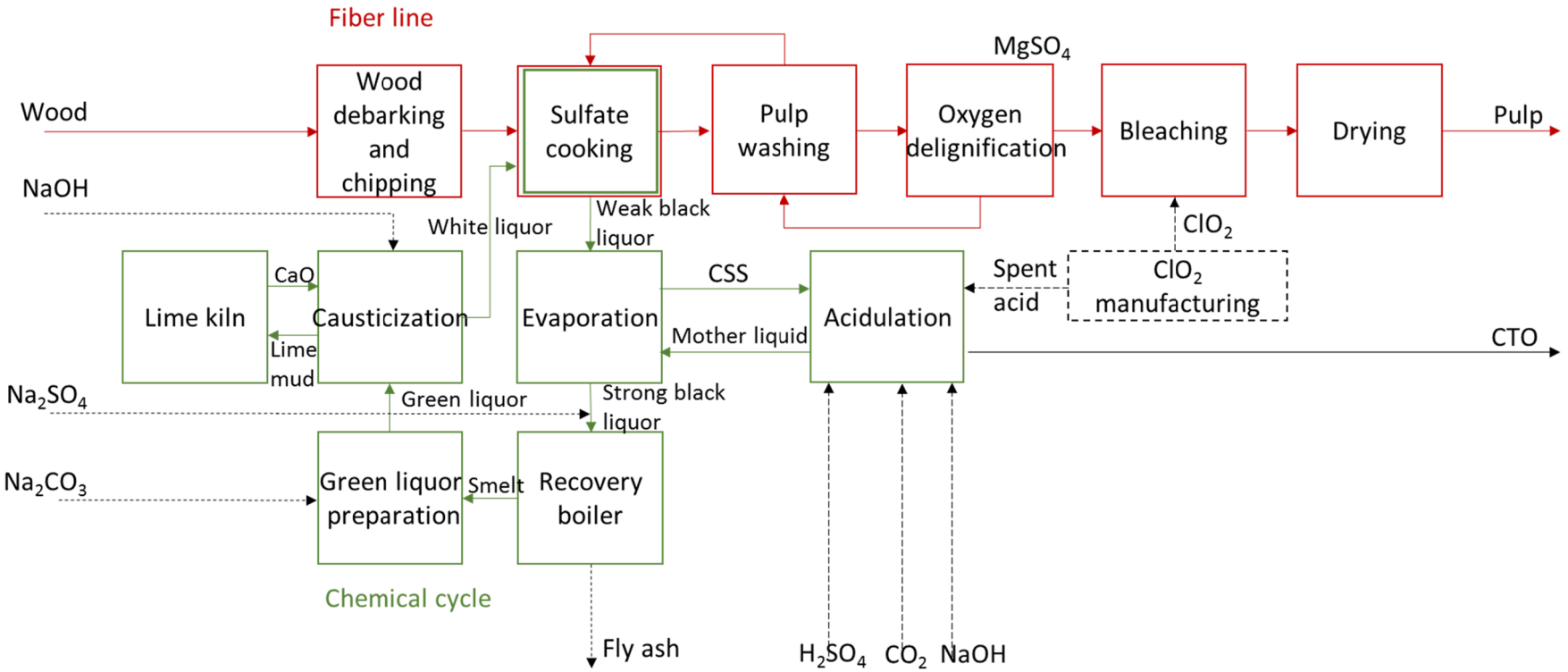

Figure 3. Kraft pulping process fiber line (red) and acidulation as a part of the chemical cycle (green).

The generation of CTO originates in the sulfate cooking of pulp. The sulfate process uses white liquor, a mixture of sodium hydroxide (NaOH) and sodium sulfide (Na_2S), as a reagent in the pulp cooking, in order to separate the cellulose fibers of wood. As a side reaction, the alkaline cooking chemicals saponify the fatty and resin acids of the wood and form crude sulfate soap, where the neutral substances from the wood, such as sterols, are dissolved.

Separation of cellulose fibers from the cooking mixture leaves a black liquor phase that contains the hemicelluloses, lignin, and other extractives of the wood, as well as used cooking chemicals and crude sulfate soap. The reacted cooking chemicals are recycled and re-used through the chemical recovery cycle of the pulp mill (see Figure 3), and black liquor is burned for energy in the recovery boiler. As a lighter phase, the foaming crude sulfate soap rises on top of the black liquor and is separated by skimming from the top of black liquor tanks. Finally, CSS is acidulated to crude tall oil, typically using sulfuric acid, sometimes also carbon dioxide or spent acid form bleaching chemical plant. [25] The yield of crude tall oil varies between 10-75 kg per air dried ton (ADt) of pulp, depending on the trees used, where they have grown and how the logs have been stored [26]. A typical CTO yield in Northern coniferous forest belt is 30-50 kg/ADt [27]. The next section, 3.1, overviews the separation of crude sulfate soap and sections 3.2, 3.3 and 3.4 present the three most typical acidulation processes, acidulation with sulfuric acid, acidulation using spent acid and pre-acidulation with carbon dioxide.

3.1 Separation of crude sulfate soap

Separation of CSS from the black liquor is an established industrial practice at the pulp mills for various reasons. First, the soap needs to be separated from the black liquor in order to prevent fouling of the evaporators. Secondly, it is removed, as feeding soap to the recovery boiler would cause control problems. [26] Thirdly, combustion of soap in the recovery boiler would bind valuable recovery boiler capacity, which is unfavorable, as the recovery boiler is the most expensive process part of the mill, and hence normally the bottle neck of the pulp production [25].

Consequently, CSS, which has risen to the top black liquor, is skimmed away from the top of liquor tanks before the liquor is fed to evaporation plant. The skimmed soap still contains some black liquor, which is separated in decanter tanks, where the black liquor falls to the bottom. [25] This second decanting phase is important in order to minimize acid consumption in acidulation, as black liquor residue in CSS increases the acid need [28].

After decantation tank, the separated CSS is pumped to acidulation plant. The acidulation can be done in batches or in a continuous process and the separation technology of tall oil can vary between decanting and centrifugal or hydrodynamic separation (HDS) processes. [25] However, considering the processing emissions calculation, only the inputs and outputs are of interest. Acidulation acid can be purchased sulfuric acid, but also spent acid from a bleaching chemical plant, chlorine dioxide (ClO_2) production, can be used. The acid need, and therefore sulfur addition, can be reduced by pre-acidulation by carbon dioxide. It would also be possible the use the salt cake, sodium bisulfite, from SO_2 scrubbers of the mill for pre-acidulation [29], but it is not known to be used in any commercial pulp mill and is therefore not studied here.

3.2 Acidulation with sulfuric acid

Crude sulfate soap is most commonly acidulated with sulfuric acid in a digester, where the temperature is raised with steam. The acidulation reaction presented below splits the soap to two fractions, upper containing the crude tall oil with free fatty and resin acids (R-COOH) as well as the dissolved neutral substances, and the lower phase containing the used chemicals (Na_2SO_4) and water.

$$2\,R-COONa + H_2SO_4 \rightarrow 2\,R-COOH + Na_2SO_4 \quad (9)$$

If black liquor has not been separated efficiently, a lignin phase is formed in the middle of the oil and water phases. The lower aqueous phase, called mother liquid (also mother liquor or brine), is returned to the evaporation plant, in order to recycle the sulfur and sodium cooking chemicals. The lignin phase is typically pumped to the chemical recovery

together with mother liquid, and burned for energy in the recovery boiler. [30] These recycled streams interlink the acidulation plant with the pulp mill chemical cycle, comparable to the concept of a refinery, presented in RED and pictured in Figure 2.

The H_2SO_4 acidulation process does not directly produce any greenhouse gases. The air emissions from acidulation consist of sulfur gases, mainly hydrogen sulfide (H_2S), which is formed in low pH from the sulfide from the black liquor residues in CSS. The sulfuric gases from the acidulation plant are led to scrubber, where they are washed with white liquor or NaOH, forming Na_2SO_4 and $NaHSO_3$ scrubber salts.

The theoretical need for H_2SO_4 in acidulation is 170 kg/ton of CTO produced, when only the soap splitting reaction is considered. Black liquor residue in soap increases the acid need [28], raising the typical value for H_2SO_4 consumption in an acidulation plant from 185 kg/ton of CTO to 240 kg /ton of CTO [27, 31]. An excess of acid is preferred in order to secure that no unreacted soap is left in the reactor. The yield of CTO is generally reported as yield per pulp produced, not per soap generated. This yield is therefore dependent on the amount of fatty and resin acids and extractives of the wood as well as the yield of soap recovery by skimming. The optimization of CTO yield from soap is mostly made by ensuring the purity of soap and minimizing the remains of black liquor in the soap phase [32].

A block diagram of the acidulation process is presented in Figure 4. First, CSS separated from black liquor is pumped to a digester with H_2SO_4. Steam is used to raise the temperature to approximately 100 °C and CTO, lignin and mother liquid phases are separated. CTO is pumped to drying tank from the top of the digester, while lignin and mother liquid are neutralized using NaOH or white liquor from the chemical cycle, and returned to the chemical recovery cycle of the mill by feeding the mixture to the evaporation plant. The drying of CTO is done using partial vacuum. [30]

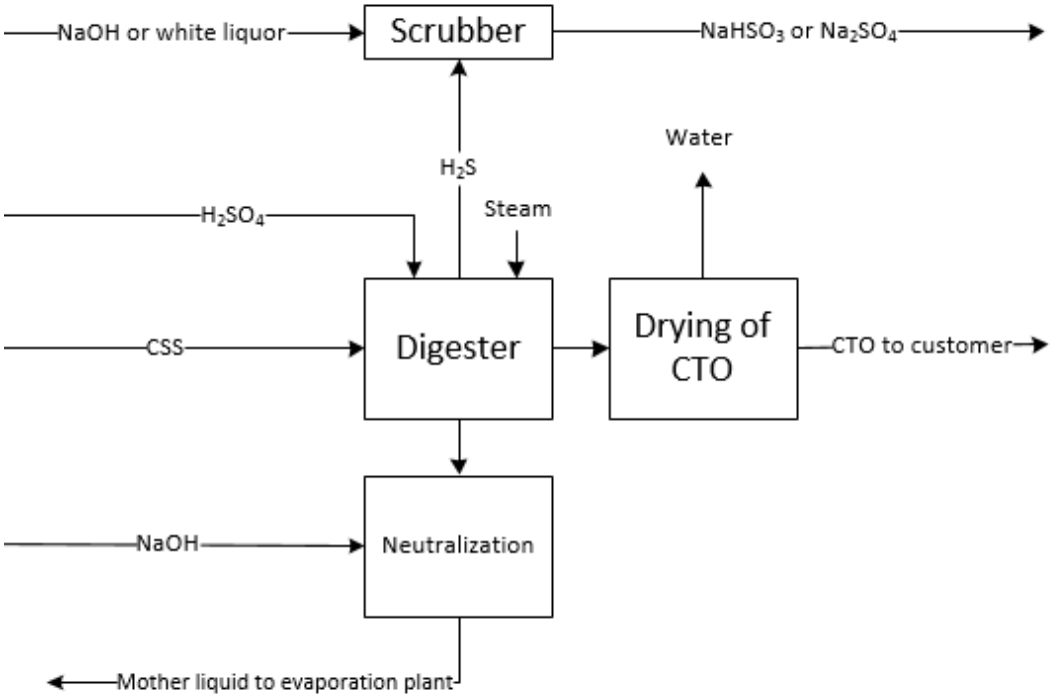

Figure 4. Block diagram of acidulation with only purchased H_2SO_4.

The inputs of the sulfuric acid acidulation process consist of CSS separated from black liquor, H_2SO_4, NaOH for neutralization and possibly gas scrubbing, process water, low pressure steam and electricity. No waste streams are generated at the acidulation plant, as the only outputs are crude tall oil and mother liquid, which is fed back to the chemical recovery cycle. The amount of water from drying of CTO is considered negligible.

3.3 Acidulation with spent acid from chlorine dioxide production

Acidulation of CSS to CTO can also be done using spent acid from the chlorine dioxide plant of the pulp mill, if such is available. Many mills produce ClO_2 for pulp bleaching on site, and it is commonly manufactured by reduction of chlorate ion with chloride ion in acidic solution. Most ClO_2 manufacturing processes use H_2SO_4 as the acid and generate Na_2SO_4 as a co-product. The residual acidic solution consists of the rests of H_2SO_4 and the produced salt, that could be in its acidic form as sodium sesquisulfate, $Na_3H(SO_4)_2$.

The spent acid solution can be used to substitute pure H_2SO_4 in acidulation, although also other options for the utilization of the spent acid exist [26]. Using spent acid instead of H_2SO_4 does not cause changes in the basic process, as seen in Figure 5. The need for spent acid is adjusted according to the pH of the soap [30], but all in all the total acid consumption is increased in comparison to using pure H_2SO_4 [28]. Spent acid consumption is dependent on the composition of the spent acid stream, and could either substitute all H_2SO_4 or be used with purchased acid. If sodium sesquisulfate is used, the consumption could be as high as 1000 kg/ ton CTO [33].

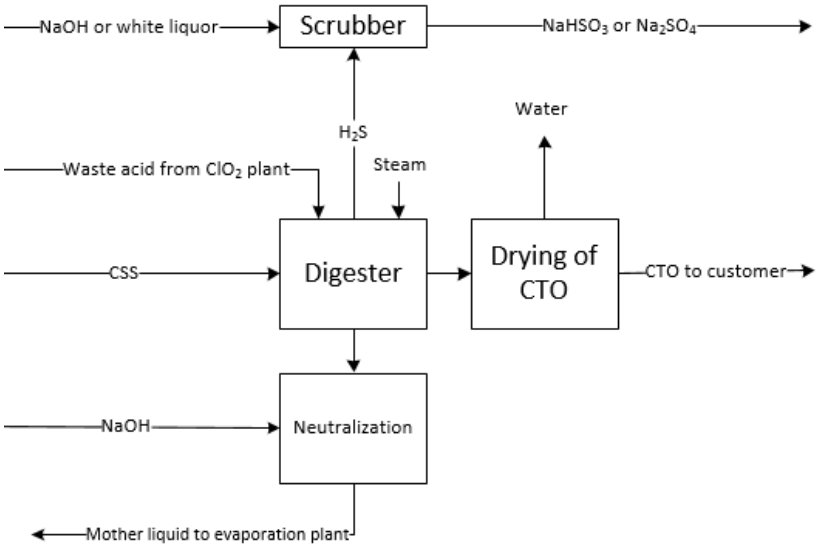

Figure 5. Block diagram of acidulation using spent acid from ClO_2 manufacturing plant.

Using spent acid in acidulation could be beneficial for the pulp mill, as the need for purchased H_2SO_4 is reduced. However, spent acid is not available in pulp mills producing unbleached pulp, or mills where ClO_2 is not manufactured on site. The usability of spent acid is also dependent on the ClO_2 generation process. The most used ClO_2 processes in Finland, Mathieson, Erco R8, AHP and SVP processes, produce spent acid without chlorine compounds, which can therefore be used for acidulation without causing corrosion problems. [18, 26, 30, 34]

3.4 Pre-acidulation with carbon dioxide

The need for sulfuric acid can be reduced by pre-acidulating (neutralizing) CSS with carbon dioxide. The acidulation process with CO_2 pre-acidulation is pictured in Figure 6. Crude sulfate soap is first pre-acidulated in a neutralization reactor, where CO_2, pressurized to 7-9 bar, is fed together with water. A typical water addition is 85-95 % of the amount of soap. CO_2 reacts with the sodium in the soap forming sodium bicarbonate ($NaHCO_3$). After neutralization the mixture is led to gas separation reactor. The reaction gases are led to scrubber and the soap is fed to soap oil decanter. Some of the H_2SO_4 is added to the soap in this stage, separating the bicarbonate water from soap oil, which is pumped further to the actual acidulation process. The acidulation process after pre-acidulation is performed equally as without pre-acidulation, only the acid need is decreased. Bicarbonate water is led back to the chemical recovery cycle together with mother liquid. [30]

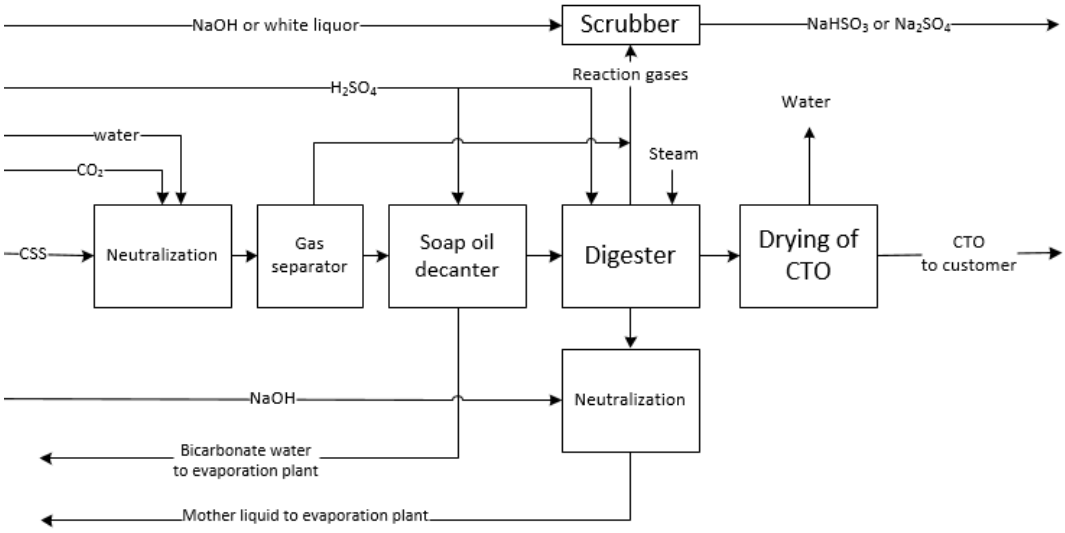

Figure 6. CSS to CTO acidulation process with pre-acidulation with carbon dioxide.

Pre-acidulation by CO_2 can be combined with acidulation by pure H_2SO_4 or spent acid from ClO_2 plant. Pre-acidulation combined with H_2SO_4 acidulation seems to be more common. About 1.63 kg of CO_2 is needed to replace 1 kg of H_2SO_4 [35]. The acid need can be reduced to half [28] when compared to the process without pre-acidulation, but the inputs are increased with CO_2, water and energy. The outputs are also increased by the bicarbonate water, which then adds to the need of water to be evaporated in the evaporation plant.

Therefore, the pre-acidulation of CSS increases the energy need at the evaporation plant in comparison to direct acidulation with H_2SO_4. As the sodium in bicarbonate water originates from the sulfate cooking and carbonates are formed in the chemical recovery anyway, the bicarbonate water addition to chemical cycle is estimated not to affect the chemical balances. The sodium bicarbonate is converted to NaOH in causticization, which returns the sodium to a usable form.

Pre-acidulation is favorable for pulp mills with high sulfidity, as it decreases the sulfur addition to the chemical cycle. It also eases the control of the acidulation plant, as the pH control is easier with CO_2 than H_2SO_4. However, if sulfur additions are in any case needed to balance the chemical cycle, replacing H_2SO_4 with CO_2 is unprofitable.

4 Sulfur and sodium balances in the kraft pulping process

The acidulation process is interlinked with the chemical recovery cycle of the pulp mill, making the pulp mill a refinery, when using specification given by sustainability scheme providers [21, 22]. As stated in RED [1], the process emissions of a fuel produced in a refinery, shall be analyzed considering the whole refinery. Hence, presuming that the same basic rules apply for raw material processing, emissions of acidulation cannot be studied simply on the acidulation plant level. The chemicals used in acidulation affect the sodium and sulfur balance of the mill, and might cause a need to remove or add these elements elsewhere. In this chapter, acidulation and other process parts affecting the sodium and sulfur balance are studied. The aim is to determine if some input or waste streams, created elsewhere in the pulp mill due to acidulation, should be included in the processing emission calculation of crude tall oil.

The chemical recovery cycle of the pulp mill, pictured in green in Figure 3, is used for recycling the valuable cooking chemicals of the pulp mill from black liquor back to the cooking of pulp. Actually, the chemical recovery cycle consists of two circuits, the calcium circuit and the alkali circuit, presented in more detail in Figure 7. To maintain a proper operation of the recovery cycle, chemical balances have to be controlled. The sulfur and sodium balance is the most important chemical balance in the kraft mill, and the sodium and sulfur cooking chemicals are recycled through the alkali recovery circle, to which acidulation plant is interlinked.

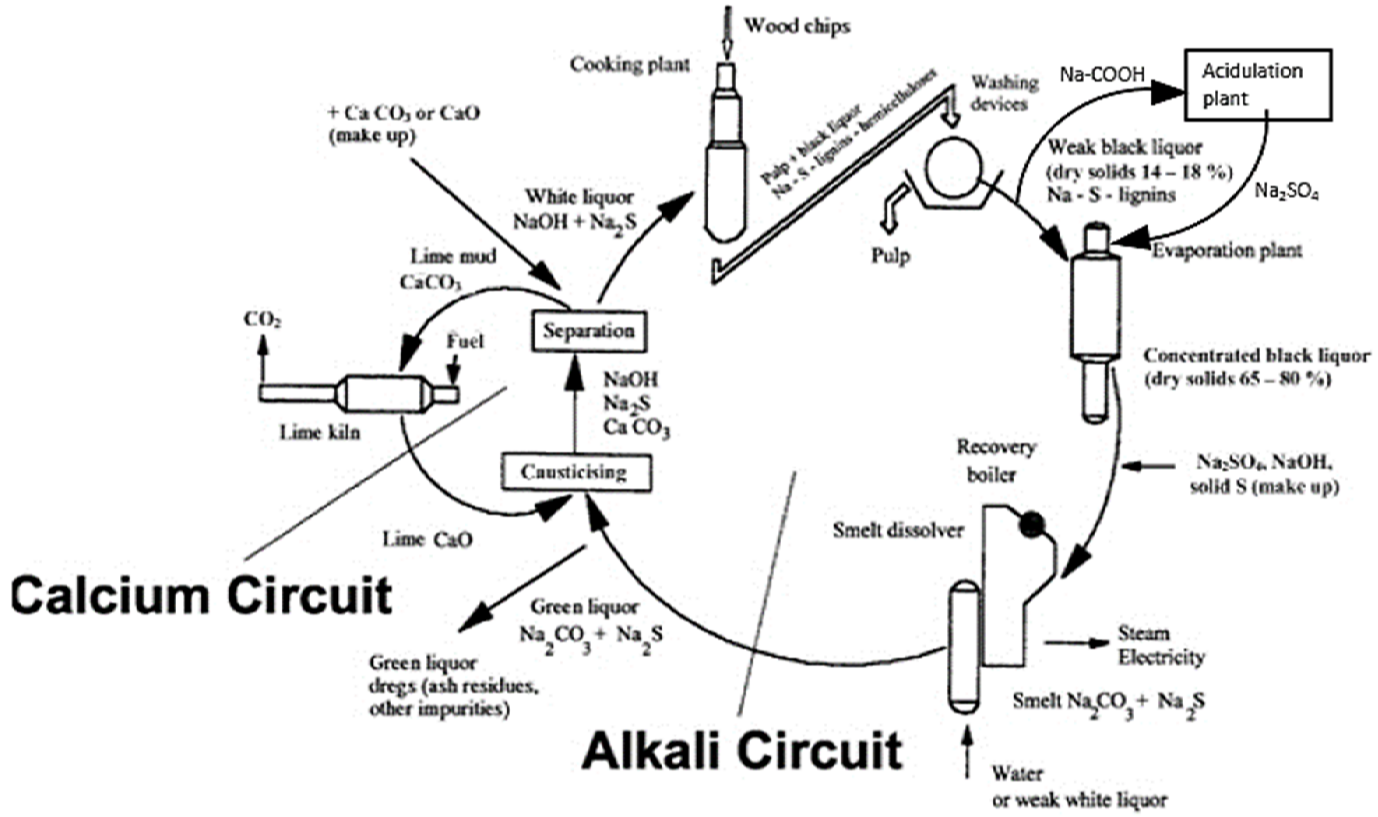

Figure 7. The calcium and alkali circuits form the chemical recovery cycle of the kraft pulp mill. Acidulation is interlinked with the alkali circuit. Adapted from [26].

As seen in Figure 7, the alkali circuit is used to recover NaOH and N_2S cooking chemicals after they have reacted with lignin and acids of the wood. First, the reacted sulfur and sodium are washed from the pulp to black liquor. Crude sulfate soap is separated from the liquor, and led to acidulation plant, where sodium reacted with the fatty and resin acids of the wood is converted to Na_2SO_4 by addition of H_2SO_4. If CO_2 pre-acidulation is used, some of the sodium is returned to the cycle in the form of $NaHCO_3$. The mother liquid, containing the acidulation chemicals, is returned to the alkali recovery cycle and fed to evaporation plant together with the black liquor. After evaporation, concentrated black liquor is burned in the recovery boiler, where sulfur and sodium are recovered in the form of Na_2S and Na_2CO_3. These salts are dissolved to weak white liquor or water, and reacted with lime (CaO) from the lime kiln to recover the chemicals needed for pulp cooking, Na_2S and NaOH. This process part is called causticizing, where also calcium carbonate, $CaCO_3$, is formed. Finally, the carbonate is separated to be converted back to CaO in the lime kiln, and NaOH and N_2S are fed back to the cooking plant.

For proper operation of the mill, the amounts of sulfur and sodium in the cycle need to be kept constant. Hence, the intakes and discharges of sodium and sulfur to and from the balance need to be equal. [25] An important indicator describing the sulfur and sodium balance in the pulp mill is sulfidity. Sulfidity indicates the share of sodium as Na_2S in comparison to the total active cooking chemicals Na_2S and NaOH. Sulfidity at modern pulp mills is normally 30-45% [25], in softwood pulping preferably 40-43%. Too low sulfidity reduces the efficiency of cooking. [27] On the other hand, if sulfidity rises too high, the sulfurous gas emissions increase, as the sulfidity searches equilibrium. This is why too high sulfidity causes problems in the gas collection system. High sulfur content might also cause corrosion in the process equipment. [25] This is why the sulfur and sodium intakes to and discharges from the chemical cycle need to be controlled.

There are always small amounts of sulfur and sodium, as well as non-process elements, such as potassium and chlorine, entering the mill with process inputs. As these cannot be let to build up in the chemical recovery circle, the recovery circle in a pulp mill can never be totally closed, as intakes need to be purged. Intakes of sulfur and sodium come from wood, water and chemicals used in the pulping process. Discharges can happen either via uncontrolled chemical losses to air, water and product streams, or in a controlled manner

by directing certain sulfur and sodium rich streams out of the chemical cycle. [31] In the next sections, first uncontrolled intakes and discharges are presented in section 4.1. Then the controllable intakes and discharges are introduced in section 4.2. Section 4.3 summarizes the typical ranges for sulfur and sodium intakes and discharges in a kraft pulp mill and discusses the control strategy of the balance.

4.1 Uncontrolled intakes and discharges of sulfur and sodium

Sulfur and sodium intakes from wood, process water or chemicals used, and discharges by air emissions or to product streams, are not controlled in the means of optimizing the chemical balance of the mill. Naturally, the efficiency of pulp washing is controlled for process reasons, and air emissions for environmental reasons, but as these variables are not changed in order to optimize the chemical balance of the mill, they are presented as uncontrolled and presumed to be constant in stabile operation of the mill.

4.1.1 Wood, water, chemicals and fuels

The wood and water used for pulping contain some sulfur, which is therefore continuously added to the chemical cycle. Non-sulfurous chemicals used in the pulp mill may contain some sulfur as impurity as well. In the EU Best available technology reference document (BREF) for the production of pulp, paper and board [26], the amount of these sulfur inputs through wood, water and chemicals is estimated to be 0.3-0.5 kg of sulfur /ADt of pulp, which is well in line with UPM pulp mill reports [27]. In a separate study, sulfur addition to the cycle with wood chips in a Finnish pulp mill has been determined to be 0.05-0.08 kg S/ADt [36], so most of the sulfur addition can be concluded to result to water and chemical impurities.

In addition, fossil fuels used in the lime kiln or recovery boiler may add sulfur to the balance. However, fossil fuels are seldom used in the chemical recovery cycle of the pulp mill in normal operation, so their effect on the chemical balance can be estimated to be negligible outside start-ups or shut-downs.

Sodium impurities in process inputs are significantly smaller than sulfur impurities. Hardwood contains negligible amounts of sodium, while the amount in softwood chips has been measured to be relatively higher, 0.03 kg Na/ADt [36]. Sodium intake through wood, water and chemicals is often estimated to be negligible [27], but values up to 0.07 kg Na/ADt are reported [31].

4.1.2 Magnesium sulfate from oxygen delignification

Magnesium sulfate ($MgSO_4$) is often added to the fiber line oxygen delignification stage, as presented in Figure 3, in order to prevent heavy metal catalyzed degradation of cellulose fibers. After delignification stage, $MgSO_4$ is dissolved in the washing water, which is then recycled back to the chemical recovery cycle, increasing the sulfur content of the cycle. [25] The estimated addition of sulfur according to the BREF document is 0.0-0.8 kg S/ADt [26].

4.1.3 Air emissions

Strong and weak odorous gases, mainly H_2S and SO_2, are collected from the recovery boiler, lime kiln and vents of the pulp mill. According to best available technology (BAT), odorous gases are either burned or scrubbed, and only residual gases are released to atmosphere. Most of the sulfur from gas collection system is thereby absorbed to the scrubber salts and removed as such, or returned to the chemical cycle. BAT-associated emission levels for total sulfur in residual gases is 0.085-0.29 kg S/ADt when the emission levels of lime kiln and recovery boiler are combined [37]. The flue gases do not contain sodium.

4.1.4 Washing of pulp

Both sulfur and sodium are lost from the chemical cycle to the fiber line (see Figure 3 in page 24), as washing of the pulp leaves a residual amount of the black liquor adsorbed to the cellulose fibers. Best available technology for kraft pulping includes highly efficient brown stock washing, which means that the chemical losses to pulp should be minimal [37]. However, no definitions of efficient washing and related chemical losses are found.

Chemical losses of washing are proposed to be of 3.49 kg Na/ADt and 0.73 kg S/ADt [31]. An older study presents higher losses, 4.5 kg Na/ADt and 1.53 kg S/ADt [38]. Recent

measurements in a Finnish pulp mill reported measured losses of 2.60 kg Na/ADt and 0.62 kg S/ADt for softwood, when the mill was facing problems with pulp washing. As these values were reported to be exceptionally high, it can be presumed that washing losses in modern mills are lower. [36] Therefore, minimum washing losses of sodium and sulfur to pulp are estimated to be 1.30 kg Na/ADt and 0.31 kg S/ADt, which are also in line with UPM internal reports [27].

4.1.5 Crude tall oil and turpentine

Crude tall oil and turpentine, which is obtained from the vapors of the sulfate cooking plant, are seldom mentioned in literature as possible outflows of sulfur and sodium. However, sulfur losses with CTO have been estimated to be 0.1-1 kg S/ton of pulp [28]. UPM internal data provides data in line with these estimations, 0.15 kg S/ADt for sulfur, and a small amount of sodium, 0.01 kg Na/ADt [27]. Significant amounts of sulfur can also be lost from the chemical cycle through turpentine. In a modern Finnish mill, 0.1 kg S/ADt was lost in turpentine stream. Turpentine did not contain any sodium. [36]

4.2 Controlled intakes and discharges of sulfur and sodium

In addition to uncontrolled intakes and discharges in a kraft pulp mill, there are several sulfur and sodium rich streams where decisions on intakes or discharges can be made. Sulfur and sodium additions of mother liquid from acidulation plant and spent acid from ClO_2 manufacturing could in theory be either sewered, used elsewhere, or lead to the chemical cycle. In addition, directing salts of SO_2 scrubbers and fly ash of the recovery boiler electrostatic precipitators away from the cycle are controlled possibilities to discharge sulfur and sodium from the balance. Finally, make-up chemicals can be added to the cycle, if sodium or sulfur content is too low.

4.2.1 Mother liquid from acidulation plant

Mother liquid from the acidulation plant is practically always led back to the chemical cycle of the pulp mill in order to recycle the cooking chemicals fed to the acidulation plant in crude sulfate soap. If recycling of mother liquid was not done, losses through soap would be 1.8-2.7 kg Na/ADt and 0.14-0.28 kg S/ADt [36, 38]. The sodium losses through

soap would be high without recovery, so the only economic solution is to return mother liquid to the chemical cycle. Disposal of mother liquid might also cause problems in wastewater treatment, as the remains of resin and fatty acids of CTO are toxic to aquatic organisms [18, 39].

In acidulation, both sulfur and sodium amounts in chemical cycle are increased as H_2SO_4 or spent acid is used for acidulation and NaOH for neutralization of mother liquid. According to one study, sulfur addition to cycle is 0.06-0.08 kg S/kg CTO if purchased sulfuric acid is used. Hence, the sulfur addition is proportional to the yield of CTO. Assuming 40 kg CTO/ADt yield the sulfur addition would be 2.4-3.2 kg S/ADt, similar to the range reported in BREF document, 2-3 kg S/ADt [26]. If spent acid from ClO_2 manufacturing is used in acidulation, the total sulfur addition is significantly increased in comparison to acidulation by pure H_2SO_4. If pre-acidulation with CO_2 is used, the sulfur addition to cycle can be reduced to half, corresponding to 1.2-1.6 kg S/kg CTO produced. [28]

Sulfur and sodium contents of the mother liquid can be calculated based on inputs to acidulation plant, and known losses to CTO and air. In the applied part of this work, typical sodium and sulfur contents of the mother liquid are determined separately for each of the three process types presented.

4.2.2 Spent acid from ClO_2 manufacturing

As described in section 3.3, chlorine dioxide is used in pulp bleaching, and is often produced in the plant area by a process producing sulfuric acid and SO_4 salts as co-products. There are several possibilities to utilize this residue stream. The spent acid stream can be used in acidulation of CTO, fed straight to the chemical cycle by feeding it to the evaporator plant with the mother liquid [36], utilized elsewhere, for example as pH adjustment in the fiber line [26, 28], or sewered [18]. The applicability of these choices is dependent on the by-products of ClO_2 process and the balance of the pulp mill.

Many processes for ClO_2 production produce some chlorine or chloride compounds as by-products. [26] Chlorine is not wanted to the chemical cycle as it could build up and induce corrosion. The most common ClO_2 processes in Finland, Mathieson, HP-A and R8

processes [34], provide chlorine free effluents. Spent acid effluent from these processes is usable for acidulation and adds both sulfur and sodium to the chemical cycle. Effluent from Mathieson process adds more sulfur to the chemical cycle than other process when equal amounts of ClO_2 are produced. [26, 30] The HP-A process produces both spent sulfuric acid and Na_2SO_4, and the R8 process produces an acidic sodium sesquisulfate salt cake [26, 40].The sodium sesquisulfate from R8 processes could be separated into H_2SO_4 and Na2SO4 [40], but is often used as such [36].

Although the spent acid is usable for acidulation, it is often preferably used for pH control of pulp bleaching [27] and not taken to the chemical cycle at all. For example, according to the environmental impact assessment of newest pulp mill planned to be built in Finland, the best solutions for optimizing the mill sulfur balance, is not to direct the spent acid to the chemical cycle at all and just try to minimize its quantity [41].

4.2.3 Scrubber salts

According to the BAT documents, odorous gases, mainly SO_2, from different parts of the pulp mill should either be burned or scrubbed in wet scrubbers [37]. As these odorous gases have high content of sulfur without any sodium, it is often favorable for sulfidity control not to let the sulfur return to the chemical balance. A common option to do this is by scrubbing the gases with NaOH and thereby producing sodium bisulfite, $NaHSO_3$, which can be utilized further outside the chemical cycle in the acidification of bleached pulp [36]. $NaHSO_3$ is a common oxidizing chemical, so if no use for it is found inside the pulp mill, it may be sold out for utilization in other processes. It could in theory be used also for pre-acidulation of sulfate soap [29], but no commercial references of this are found [25]. SO_2 can also be scrubbed using white liquor, when Na_2SO_4 is produced.

If scrubber salts are washed with white liquor and returned to the chemical cycle, no losses through scrubber salts exist. However, when $NaHSO_3$ for other uses has been produced the sulfur losses from the cycle have been 0.6 kg S/ADt. No sodium losses are generated if external NaOH is used for scrubbing, but 0.7 kg Na/ADt losses through scrubber salts are reported when white liquor is used. [36]

4.2.4 Make-up chemicals

If sulfur or sodium levels in chemical cycle are too low, the balance can be corrected by adding make-up chemicals to the cycle. The quantities of needed sodium and sulfur make-up are dependent on all other intakes and discharges of sodium and sulfur, and the make-up chemicals are the most flexible way for balancing chemical deficit in the recovery cycle.

Traditionally the most common make-up chemical has been Na_2SO_4, but in modern high sulfidity mills, additional sulfur is often not needed, and Na_2SO_4 has been replaced with NaOH or Na_2CO_3 [18, 28]. NaOH can be added in several points of the chemical cycle [25, 28], Na_2SO_3 is added before caustizing [28].

4.2.5 Fly ash from the electrostatic precipitators

Excessive sulfur and sodium levels in the chemical cycle can be reduced by removing salts, mainly Na_2SO_4, from the fly ash collected by the electrostatic precipitators of the recovery boiler. In modern mills, an excess of sodium is not typical without concurrent excess of sulfur. Even more typically, only sulfur excess exists. Fly ash removal always diminishes the amounts of both sulfur and sodium, and if the reason for fly ash removal is sulfur excess, removed sodium has to be replaced by adding NaOH or Na_2CO_3 make up to the balance. [25]

In addition to controlling sulfur and sodium balance, fly ash removal is a good way to purge non-process elements, such as potassium and chlorine, out of the chemical cycle, as they concentrate in the recovery boiler. Typically, some fly ash is always removed for this reason. A modern way to do this is by using ash-leaching technologies, where non-process elements are dissolved to acidic water and directed to waste water treatment, as most Na_2SO_4 stays in solid form and can be recycled as a slurry back to the recovery cycle. Na_2SO_4 losses to wastewater are around one third of the total amount for maximal removal of non-process elements. [42] In this work, the minimum fly ash discharge is estimated to be 0.132 kg S/ADt as Na_2SO_4, based on 33% fly ash loss to wastewater from the total amount of sulfur in fly ash, 0.4 kg S/ADt [28].

If ash-leaching is not used, the fly ash can be removed by dissolving it into water and directing it to waste water treatment [25]. Fly ash from pulp mills has also been

successfully utilized as a hardener for filling mine cavities and as a filler in asphalt mass [43]. It can also be granulated and recycled back to the forest as a fertilizer [44].

4.3 The impact of acidulation in a typically balanced pulp mill

As concluded in earlier chapters, sewering mother liquid from acidulation is not a practical option for pulp mills, and therefore the sulfur and sodium additions from acidulation to the chemical balance have to be considered a default intake. Spent acid from ClO_2 manufacturing on the other hand has other uses outside the chemical cycle and not directing it to the chemical cycle is a preferred choice in many modern pulp mills, if it is not used for acidulation. In the probable case, that spent acid is not taken to the chemical cycle, acidulation intake forms a major part of all sulfur input to the balance. The role of acidulation as a sulfur intake becomes even more emphasized when no external sulfur containing fuels are used in the pulp mill.

Table 2 summarizes the ranges found for typical kraft mill sodium and sulfur intakes and discharges. According to conclusions drawn, the more probable ends of the ranges are marked with bolded values. These are zero intakes from fuels and spent acid, and zero discharge of sodium in scrubber salts, when external NaOH is used for scrubbing. By estimation, a minimum of 0.13 kg S/ADt as Na_2SO_4 has to be removed from the fly ash of electrostatic precipitators in order to purge non-process elements from the cycle. [18, 31] Increasing fly ash removal or adding make-up chemicals are the simplest ways to control the sulfur and sodium balances of the mill and the quantities vary depending on other uncontrolled intakes and discharges.

The impact of acidulation on the operation of the pulp mill is also dependent of the other intakes and discharges of sulfur in the mill. Depending on the pulping process and its integrations affecting the chemical balance, acidulation of CSS to CTO could lead to excess amounts of sulfur in the balance, increase the need for fly ash removal from the electrostatic precipitators and therefore add the need for make-up NaOH. However, if discharges from the chemical cycle are greater than intakes without acidulation, the sulfur addition from mother liquid can also be necessary for balancing the pulp mill. If that case,

sulfur addition from acidulation reduces the need for sulfur containing make-up chemicals.

Table 2. The ranges of sulfur and sodium intakes and discharges in a typical kraft pulp mill. Bolded values are considered more typical than the other end of the range. Make-up chemical intake and fly ash discharge are altered so that the intakes and discharges are balanced.

		Sulfur		Sodium	
		Range	**References**	**Range**	**References**
Intakes in a kraft mill (kg/ADt)	**Wood, water and chemicals**	0.3-0.5	[26, 34]	0.0-0.07	[27]
	$MgSO_4$ from delignification	0.0-0.8	[26, 34]	0.0	[34]
	Fuels	**0.0**-2.0	[26]	0.0	[34]
	ClO_2 waste acid	**0.0**-15.0	[26]	**0.0**-21.5	[26] as Na_2SO
	Acidulation of CTO	1.2-3.2	[26, 27]	0.0-0.3	[27]
	pH adjustment /Make-up chemicals		calculated		calculated
Discharges in a kraft mill kg/ADt)	**Air emissions**	0.05-1.0	[35, 41]	0.0	[44]
	Scrubber salts	0.0-0.6	[34]	**0.0**-0.7	[36]
	Fly ash from electrostatic precipitators	0.13-	[28, 42] calculated	0.19-	[28, 42] calculated
	Washing losses in fiber line	0.3-1.5	[38]	1.3-4.5	[38]
	Crude tall oil	0.1-1.0	[27]	-0.01	[27, 36]
	Turpentine	0.0-0.1	[36]	0.0	[36]

In conclusion, acidulation process is strongly integrated with the pulp mill and therefore the effects of acidulation on the chemical balance cannot be excluded from the calculations of acidulation emissions. Moreover, the operation of the chemical cycle is optimized as a unity in order to optimize the pulp production process and changes in some parts of the cycle could affect the control strategy of others. For these reasons, a model of a typical pulp mill balance is not easy to define, and conclusions should not be based on results obtained using single starting values. In the next part of the work, the emissions of acidulation are hence calculated with estimated typical values, and studied over the ranges presented here.

APPLIED PART

5 Defining the acidulation process emissions in a kraft pulp mill

The literature part summarized the policies and guidelines for the process emission calculation and described the typical acidulation processes and their effect on the chemical balance of the pulp mill. This chapter first presents a method for calculating process emissions for acidulation, based on the information gathered, which was the first objective of this work. Then, the method is used to calculate the acidulation emissions of the three most typical process types presented and to analyze the sensitivity of the results to changes in the acidulation process and pulp mill operation. Conclusions on whether the acidulation emissions can be separated from the pulp production emissions are drawn and deductions made regarding the residue status of CTO, based on the sensitivity analysis and EU legislation presented in the previous part. The role of acidulation process on defining the status of CTO is discussed in more detail in chapter 6 and conclusions are summarized in chapter 7.

In this chapter, section 5.1 first presents the definitions of system boundaries and related input and waste streams that need to be considered in the emission calculations of acidulation. Section 5.2 lists the presumptions for calculations made, including the balances and control strategy for the reference pulp mill used in calculations, based on information gathered in chapter 4, and balances for the three typical acidulation processes, presented in chapter 2.6. The calculation and results are presented in section 5.3 and finally, the sensitivity analysis, which provides the most important results of this work, is made in section 5.4.

5.1 System boundary and calculation method

Acidulation process is directly interlinked with the pulp mill chemical recovery cycle and affects the sulfur and sodium balance of the pulp mill, as concluded in the literature part. This causes a challenge to the emission calculation, because defining the system boundary is not as straightforward, as it would be for a separate process.

According to the EU Renewable Energy Directive as well as voluntary and national certification schemes, the unit for the analysis of process emissions for interlinked processes should be the refinery. This rule is set for calculating the process emissions of biofuel production, but as no other specifications are given for any feedstock processing, it is concluded that same rules apply throughout the whole production chain. In this context, the refinery is the pulp mill. Consequently, emission allocation should be done only for products exiting the balance area, when no more interlinkages exist between the process parts. Thus, according to the EU policy, emissions of acidulation should not have to be defined separately. This guideline is likely given, as the separation of emissions between different process parts is not always possible.

Despite the initial controversy, the process emissions of acidulation can be calculated with certain presumptions, keeping the system boundary set around the pulp mill, as defined for refineries. In this approach, the emissions of a pulp mill with acidulation plant are compared to the emissions that the pulp mill would have without the acidulation plant. The pulp mill without the acidulation plant is assumed identical to the one with acidulation, with the exception, that instead of processing CSS to CTO, CSS is directed outside the pulp mill as such. Although CSS could be taken to acidulation for example to another pulp mill, this is mainly a theoretical approach, in order to allow calculation of the emissions from the creation of CSS to the creation of CTO. Combustion of CSS is not regarded as a reference, as it is not comparable to a process where CTO can still be further utilized.

Hence, the acidulation process emissions are calculated as pictured in Figure 8. The approach is based on calculating

$$EM_C = EM_{A,total} - EM_{B,total}, \quad (10)$$

where

- EM_C is the total emissions caused by the acidulation process in the whole pulp mill,
- $EM_{A,total}$ is the greenhouse gas emissions of a whole pulp mill with an integrated acidulation process and
- $EM_{B,total}$ is the greenhouse gas emissions of a whole pulp mill without an acidulation process, CSS being directed outside the mill.

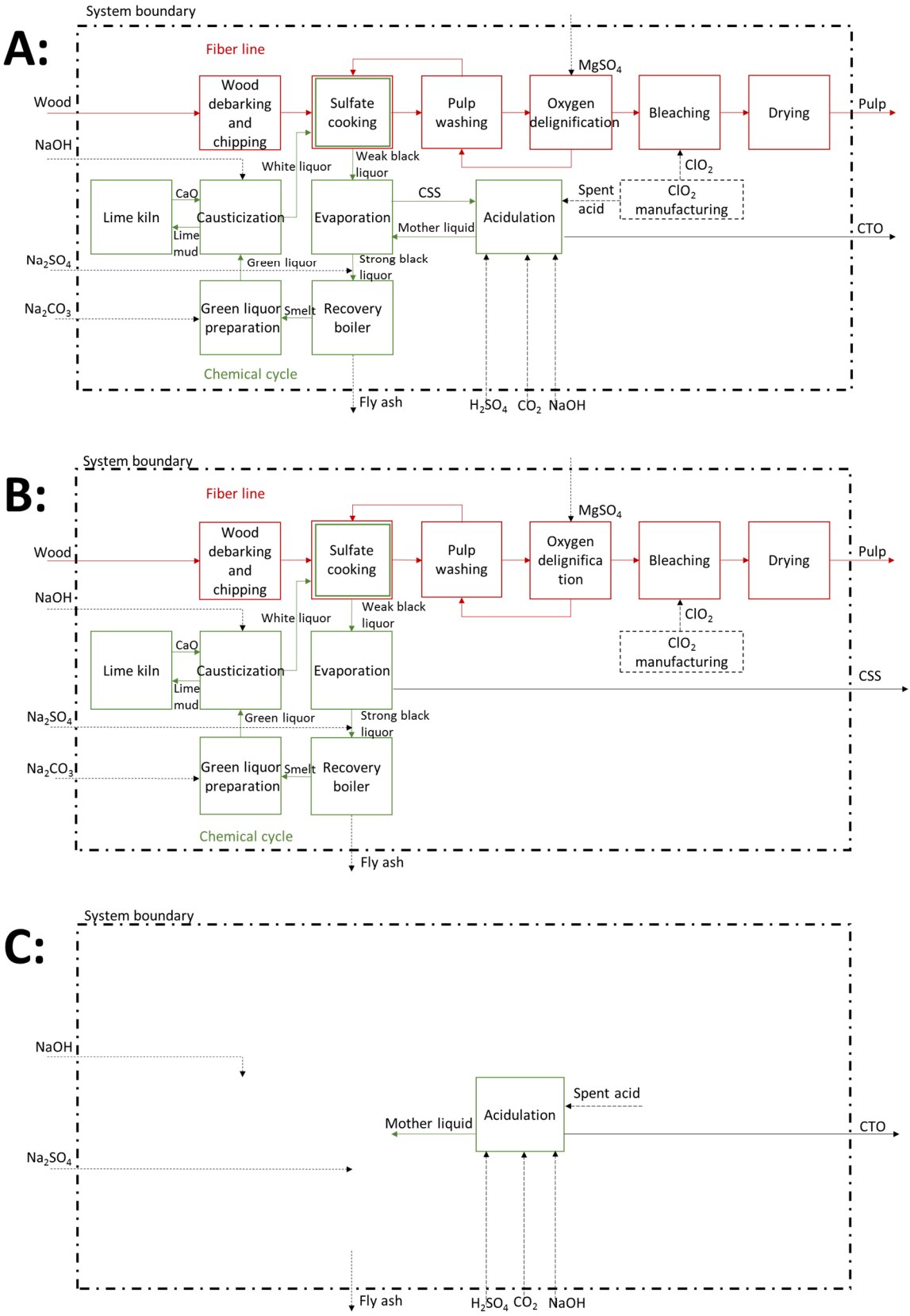

Figure 8. A-B=C. Emissions created by acidulation in a pulp mill are calculated by substracting the emissions of a pulp mill without acidulation (B) from the emissions of a pulp mill with acidulation (A).

In order to simplify the calculations, the emissions of the pulp mill A, EM_A and pulp mill B, EM_B do not have to be determined in totality. As the interest is in their remainder, the emissions of all streams that are equal in mill A and mill B can be excluded from the calculations, as their effect on EM_C is zero. Hence, only the difference is intakes and discharges form the pulp mills A and B is estimated. According to information gathered in chapters 3 and 4, the intake and discharge streams affected by acidulation are acidulation inputs and in the chemical recovery cycle the make-up chemical need and fly ash discharge need. In addition, electricity and steam use of the whole mill are increased in mill A, compared to mill B without acidulation. These streams, except the difference energy need, are all pictured for process C in Figure 8 and the calculation is based on these differences.

When excluding the emissions that stay constant in both mill A and mill B, the calculation reduces to:

$$EM_C = EM_{A,total} - EM_{B,total} = EM_A - EM_B, \quad (11)$$

where

- EM_C is the total emissions caused by the acidulation process in the whole pulp mill,
- EM_A is the greenhouse gas emissions of the pulp mill with an integrated acidulation process when only the acidulation inputs, make-up chemical need, fly ash discharge and energy consumption are considered and
- EM_B is the greenhouse gas emissions of a whole pulp mill without an acidulation process, CSS being directed outside the mill, when only the make-up chemical need, fly ash discharge and energy consumption are considered.

The total emissions caused by acidulation, EM_C, are therefore determined by the inputs in acidulation, and in the changes of controlled intake and discharge of sulfur and sodium in the chemical recovery cycle of the pulp mill. The chemical balances are controlled by adding make-up chemicals, Na_2SO_4 or NaOH, if there is a deficit of sulfur or sodium, and by removing fly ash from electrostatic precipitators of the recovery boiler, if there is surplus of sulfur or sodium. All these emissions are calculated and allocated to CTO exiting the process, as pictured in Figure 9.

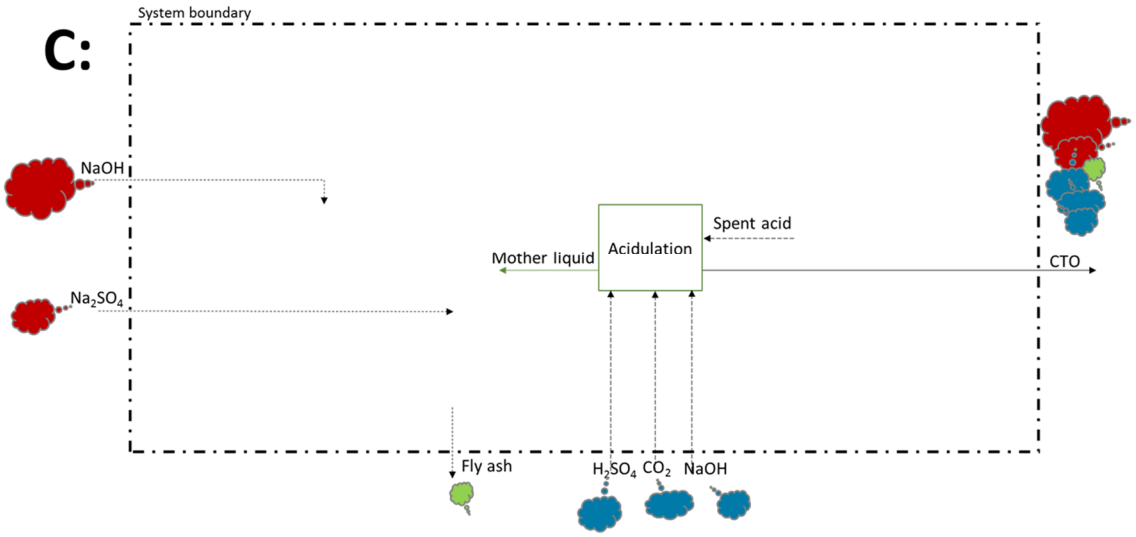

Figure 9. The emissions allocated to crude tall oil are calculated as a sum of emissions created by acidulation inputs (blue clouds), emissions created or reduced by the change (EM_A-EM_B) in the need of make-up chemicals (red clouds) and emissions created by the change (EM_A-EM_B) in the generation of wastewater treatment of the fly ash slurry (green cloud). In addition, the change in the energy consumption of the mill is considered.

The emissions of acidulation for process C in Figure 8 can be calculated following Equations 4 to 8 as:

$$e_{p,C}\left[\frac{\mathrm{kgCO_2}}{\text{ton CTO}}\right] = \left(EM_{electricity\ consumption,A} - EM_{electricity\ consumption,B}\right) + \left(EM_{heat\ production,A} - EM_{heat\ production,B}\right) + \left(EM_{inputs,A} - EM_{inputs,B}\right) + \left(EM_{waste\ water,A} - EM_{waste\ water,B}\right) \quad (12)$$

where

emission caused by the consumption of electricity for each case is

$$EM_{electricity\ consumption,i}\left[\frac{\mathrm{kgCO_2}}{\text{ton CTO}}\right] = electricity\ \left[\frac{\mathrm{kWh}}{\text{ton CTO}}\right] * \mathrm{EF}_{\text{electricity used in the pulp mill}}\left[\frac{\mathrm{kgCO_2}}{\mathrm{kWh}}\right], \quad (13)$$

emission caused by the production of heat, equal to the internal consumption of low pressure steam is

$$\mathrm{EM}_{\text{heat production,i}}\left[\frac{\mathrm{kgCO_2}}{\text{ton CTO}}\right] = \text{fuel consumption}\ \left[\frac{\mathrm{kg}}{\text{ton CTO}}\right] * \mathrm{EF}_{\text{fuel used in the pulp mill}}\left[\frac{\mathrm{kgCO_2}}{\mathrm{kg}}\right], \quad (14)$$

emission caused by the production of inputs used in processing is

$$\mathrm{EM}_{\mathrm{inputs,i}}\left[\frac{\mathrm{kgCO_2}}{\mathrm{ton\ CTO}}\right] = \mathrm{H_2SO_4}\ \left[\frac{\mathrm{kg}}{\mathrm{ton\ CTO}}\right] * \mathrm{EF}_{\mathrm{H_2SO_4}}\left[\frac{\mathrm{kgCO_2}}{\mathrm{kg}}\right] + \mathrm{Spent\ acid}\ \left[\frac{\mathrm{kg}}{\mathrm{ton\ CTO}}\right] * \mathrm{EF}_{\mathrm{Spent\ acid}}\left[\frac{\mathrm{kgCO_2}}{\mathrm{kg}}\right] + \mathrm{CO_2}\ \left[\frac{\mathrm{kg}}{\mathrm{ton\ CTO}}\right] * \mathrm{EF}_{\mathrm{CO_2}}\left[\frac{\mathrm{kgCO_2}}{\mathrm{kg}}\right] + \mathrm{Process\ water}\ \left[\frac{\mathrm{l}}{\mathrm{ton\ CTO}}\right] * \mathrm{EF}_{\mathrm{Process\ water}}\left[\frac{\mathrm{kgCO_2}}{\mathrm{l}}\right] + \mathrm{NaOH}\ \left[\frac{\mathrm{kg}}{\mathrm{ton\ CTO}}\right] * \mathrm{EF}_{\mathrm{NaOH}}\left[\frac{\mathrm{kgCO_2}}{\mathrm{kg}}\right] + \mathrm{Na_2SO_4}\ \left[\frac{\mathrm{kg}}{\mathrm{ton\ CTO}}\right] * \mathrm{EF}_{\mathrm{Na_2SO_4}}\left[\frac{\mathrm{kgCO_2}}{\mathrm{kg}}\right] \quad (15)$$

and emission caused by the treatment of waste waters from the process is

$$EM_{waste\ water,i} = waste\ water\ \left[\frac{m^3}{ton\ CTO}\right] * \mathrm{EF}_{\mathrm{waste\ water}}\left[\frac{kgCO_2}{m^3}\right]. \quad (16)$$

For comparison, Figure 10 presents an alternative way of defining the system boundary for acidulation process emissions. This approach would ignore the emissions created or saved in the chemical cycle due to acidulation and is not valid for an interlinked process. In order to demonstrate the difference between the two approaches, the results for emissions calculation in section 5.3 are presented also for this system boundary setting.

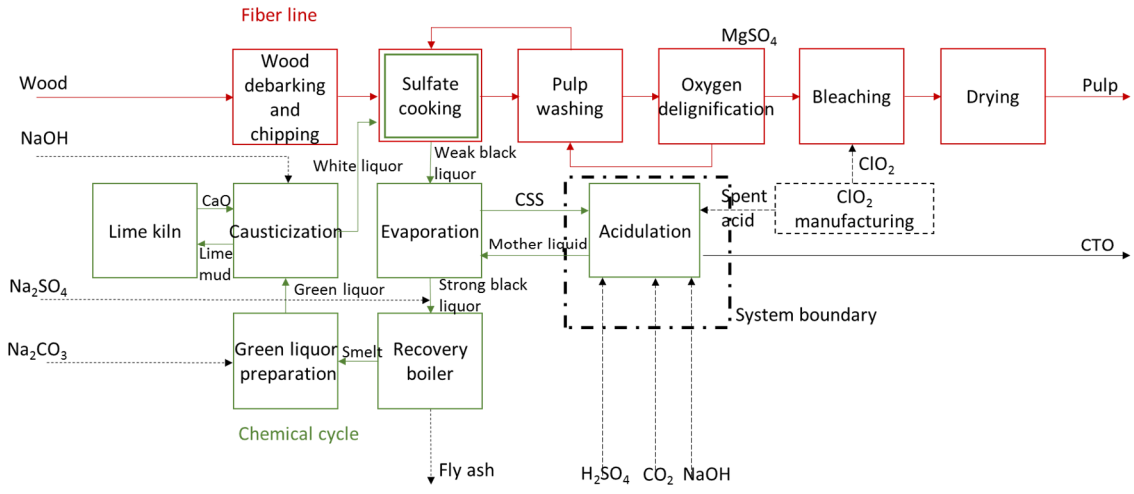

Figure 10. System boundary set around the acidulation process would exclude the effects of acidulation to the chemical cycle from the emission calculation. This system boundary setting is presented only for comparison.

5.2 Basis for calculation

The emission calculations are conducted according to equation 11 for three different cases, as emissions of the mill with acidulation (EM_A) are dependent on the acidulation process used. Later in this this work

- A_1 refers to the pulp mill with acidulation by sulfuric acid (H_2SO_4 process),
- A_2 refers to the pulp mill with acidulation by spent acid from ClO_2 production (spent acid process),
- A_3 refers to the pulp mill with pre-acidulation by carbon dioxide and final acidulation by sulfuric acid (CO_2 + H_2SO_4 process) and
- B refers to the pulp mill without acidulation process, CSS being directed outside the mill.

Excluding the varying make-up and fly ash removal needs, the operation of the mill is estimated to be similar with and without acidulation. Therefore, the presumptions made for the reference pulp mill, presented in the next section, apply for all mills A_1, A_2, A_3 and B. All values used in calculations are scaled for one ADt of pulp and further for one ton of produced CTO. Therefore, all the calculations are independent of mill or acidulation process capacities.

5.2.1 Reference pulp mill chemical recovery cycle

The reference pulp mill is a model of a typical kraft pulp mill, built based on literature and UPM internal data presented in chapter 4 and summarized in Table 2. Acidulation emissions, EM_C, are dependent only on the changes in the chemical recovery cycle of the pulp mill, and hence presumptions on other areas are not relevant. All calculations on the emissions of mills A_1, A_2, A_3 with acidulation and mill B without acidulation, are based on the same reference mill chemical balances. The following presumptions are made for the reference mill:

- All fuels used in the lime kiln and recovery boiler are sulfur free, bio based and the mill is self-sufficient in energy.

- Spent acid or salt cake from ClO_2 manufacturing is directed to the chemical recovery cycle only if it is utilized in acidulation.
- In the chemical cycle, the sulfur and sodium inputs are equal to the discharges, so that the pulp mill is balanced.
- Excess of sulfur or sodium is purged by removing fly ash from the electrostatic precipitators of the recovery boiler. In the calculations, fly ash is considered to be Na_2SO_4 and the removal rate at least 0.13 kg S/ADt in order to purge non-process elements from the cycle. Fly ash is removed to waste water treatment as a solution or slurry, containing 200 kg Na_2SO_4/m^3.
- Deficit of sulfur and sodium is compensated by adding Na_2SO_4 and NaOH to the chemical cycle as make-up chemicals.
- Sulfurous gas scrubbing is made with purchased NaOH and the resulting salt is utilized outside the chemical cycle. Therefore, no sodium is discharged through scrubber salts.
- If no other presumption is made, all sulfur and sodium intakes and discharges are set to 50% of their range, meaning the average of minimum and maximum value defined in Table 2.

Table 3 compiles the intakes and discharges of sulfur and sodium for the reference pulp mill described above. Values affected by the acidulation are calculated for each process separately. The values for crude sulfate soap discharge are used only for mill B without crude tall oil production. Correspondingly, the values for CTO discharge are used only for mills A_1, A_2, A_3.

Table 3. Intakes to and discharges from the chemical balance of the reference pulp mill, based on the typical ranges presented in Table 2.

	Reference pulp mill	Sulfur	Sodium	Notes
Intakes to the pulp mill (kg/ADt)	Wood, water and chemicals	0.40	0.04	50% of range
	MgSO4 from delignification	0.40	0.00	50% of range
	Fuels	0.00	0.00	sulfur free fuels used
	ClO2 waste acid	0.00	0.00	not directed to chemical cycle
	Acidulation of CTO			calculated separately
	pH adjustment /Make-up chemicals			calculated separately
Discharges from the pulp mill (kg/ADt)	Air emissions	0.19	0.00	50% of range
	Scrubber salts	0.30	0.00	50% of range for S, ext. NaOH used
	Fly ash from electrostatic precipitators			calculated separately, min. 0.13 kg S/ADt
	Washing losses in fiber line	0.90	2.90	50% of range
	Crude sulfate soap	0.20	2.25	50% of range for mill B *without* acidulation, else 0
	Crude tall oil	0.55	0.01	50% of range for mills A_1, A_2 and A_3 *with* acidulation, else 0
	Turpentine	0.05	0.00	50% of range

5.2.2 Acidulation plant

The greenhouse gas emissions of three different acidulation processes, compared to emissions of mill B without acidulation, are calculated presuming that the processes are integrated with the reference pulp mill chemical recovery cycle presented in the previous section. The following presumptions were made for all three acidulation processes in mills A_1 (mill with H_2SO_4 process), A_2 (mill with spent acid process) and A_3 (mill with CO_2 + H_2SO_4 process):

- CTO yield is 40 kg/ADt, which is 50% of the typical range, 30-50 kg/ADt.
- Mother liquid is always returned to the chemical cycle.

- H_2SO_4 and CO_2 used for acidulation are purchased as normal market chemicals, not produced within the pulp mill integrate area.
- Emissions of water from drying of CTO are negligible in the emission calculation and can be ignored.
- Emissions of unreacted CO_2 when pre-acidulation is used (mill A_3) are negligible in the emission calculation and can be ignored.
- The effect of acidulation on the total sulfur loss through SO_2 and TRS emissions to scrubber salts and air is negligible and can be ignored.
- In the chemical recovery cycle, only sulfur and sodium balances and energy consumption of the evaporation plant due added water are affected by acidulation.
- Spent acid from the ClO_2 manufacturing is sodium sesquisulfate, $Na_3H(SO_4)_2$ when spent acid is used (mill A_2).

The estimated uses of acidulation inputs are compiled to Table 4. Acid consumption in H_2SO_4 process of the mill A_1 is estimated to be 50% of the range 170-240 kg H_2SO_4 /ton of CTO [27, 31]. In CO_2 + H_2SO_4 process of the mill A_3, half of the acid need is substituted with CO_2, with the ratio 1.63 kg CO_2/ kg H_2SO_4 [44]. Sodium sesquisulfate need in mill A_2 is set 1000 kg /ton CTO [33]. The amounts of process water and NaOH uses are based on UPM internal reports [27]. In addition to NaOH, white liquor is used in acidulation plant, but as it comes from the chemical recovery cycle and is returned there in equal amounts, it can be excluded from the analysis.

Table 4. Estimated inputs of the three most common acidulation processes.

Inputs	**H_2SO_4 process (mill A_1)**	**Spent acid process (mill A_2)**	**CO_2 + H_2SO_4 process (mill A_3)**	**Unit**
H_2SO_4	205	0	103	kg/ ton CTO
Spent acid, $Na_3H(SO_4)_2$		1000		kg/ ton CTO
CO_2	0	0	167	kg/ ton CTO
Process water	500	500	2500	l/ ton CTO
NaOH	5	5	5	kg/ ton CTO

5.2.3 Emission factors

Emissions created during the production and distribution of process inputs and in the treatment of waste streams are taken into account by using emission factors, which are defined separately for each input and waste stream. The emissions factors used in this work are listed in Table 5. The factors for purchased chemicals and wastewater treatment are obtained from Biograce [24] and Ecoinvent [23] databases, which are generally accepted providers for lifecycle analysis data.

For spent acid, electricity and steam, zero emission factors are used. For spent acid, this is due to EU greenhouse gas calculation rule, where wastes and residues have zero emissions in the point where they are generated [1]. Spent acid from ClO_2 manufacturing is a residue stream generated at the pulp mill, as according to the definition of residue, the primary aim of the ClO_2 manufacturing is to produce ClO_2, not spent acid. The process has neither been modified in order to produce spent acid. [5, 7] Electricity and steam are produced within the pulp mill in the combustion of black liquor. Therefore, the emission factor for average regional electricity mix is not used and according to RED, emissions from the bioliquid or fuel in use are regarded as zero. No emissions are allocated to black liquor in the pulp mill, as it is considered a residue of pulp production [1, 12].

Table 5. Emission factors used in this work.

		Emission factor	Unit	Reference
Inputs	H_2SO_4	0.2100	kgCO2eq/kg	Biograce, 2011 [24]
	Spent acid	0.0000	kgCO2eq/kg	waste/residue stream
	CO_2	0.8159	kgCO2eq/kg	Ecoinvent 2.2 [23]
	Process water	0.0003	kgCO2eq/l	Biograce, 2011 [24]
	NaOH	0.4700	kgCO2eq/kg	Biograce, 2011 [24]
	Steam	0.0000	kgCO2eq/MJ	Bioenergy produced at plant
	Electricity	0.0000	kgCO2eq/kWh	Bioenergy produced at plant
	Na_2SO_4 purchased	0.1400	kgCO2eq/kg	Ecoinvent 2.2. [23]
Waste	Wastewater	0.4636	kgCO2eq/m^3	Ecoinvent 2.2 [23]

5.3 Calculation of greenhouse gas emissions of acidulation processes

Chemical balances, input and waste streams, and resulting emissions, were calculated for four cases, first for the reference model pulp mill without acidulation plant (B) and then for the model pulp mill integrated with each of the three acidulation processes (A_1, A_2, and A_3). Section 5.3.1 presents the material balances calculated for each case and section 5.3.2 describes the final emission calculations and presents the results.

5.3.1 Pulp mill balances

The pulp mill balances were completed using already defined input and output values, presented in Table 3, and calculating the intakes from acidulation of CTO separately for each case. Then the pulp mill intakes and discharges were balanced by increasing fly ash removal and adding make-up chemicals if needed.

For the pulp mill without acidulation process (B) the sulfur and sodium intakes from acidulation are zero. For the mills with acidulation processes (A_1, A_2 ,A_3) the sulfur and sodium additions were calculated according to inputs presented in Table 4.

The sulfur intake from acidulation of CTO to the chemical balance is

$$\mathrm{S}_{\mathrm{acidulation,Ai}}\left[\frac{\mathrm{kg}}{\mathrm{ADt}}\right] = \left(\frac{\mathrm{H2SO4}}{\mathrm{M}_{\mathrm{H2SO4}}} + \frac{\mathrm{Na3H(SO4)2}}{\mathrm{M}_{\mathrm{Na_3H(SO_4)_2}}}\right) * \frac{\mathrm{M_S}}{1000} * \mathrm{yield}_{\mathrm{CTO}}, \quad (17)$$

where

H_2SO_4 is the mass of H_2SO_4 used in acidulation as kg/ton CTO (Table 4),

$\mathrm{M_{H2SO4}}$ is the molar mass of H_2SO_4, 98.08 g/mol,

$Na_3H(SO_4)_2$ is the mass of $Na_3H(SO_4)_2$ used in acidulation as kg/ton CTO (Table 4),

$\mathrm{M_{Na3H(SO4)2}}$ is the molar mass of $Na_3H(SO_4)_2$, 262.11 g/mol,

$\mathrm{M_S}$ is the molar mass of sulfur, 32.07 g/mol and

$\mathrm{yield_{CTO}}$ is the yield of crude tall oil, 40 kg/ADt.

Equally, the sodium intake from acidulation of CTO to the chemical balance is

$$\mathrm{Na}_{\mathrm{acidulation,Ai}}\left[\frac{\mathrm{kg}}{\mathrm{ADt}}\right] = \left(\frac{\mathrm{NaOH_{acidulation}}}{\mathrm{M_{NaOH}}} + \frac{\mathrm{Na3H(SO4)2}}{\mathrm{M_{Na3H(SO4)2}}}\right) * \frac{\mathrm{M_{Na}}}{1000} * \mathrm{yield}_{\mathrm{CTO}}, \quad (18)$$

where

$NaOH_{acidulation}$ is the mass of NaOH added in acidulation as kg/ton CTO (Table 4),

M_{NaOH} is the molar mass of sodium hydroxide, 40.00 g/mol and

M_{Na} is the molar mass of sodium, 22.99 g/mol.

The resulting intakes from acidulation of CTO for the acidulation processes are presented in Table 6.

Table 6. Sulfur and sodium intakes of different acidulation processes and reference without acidulation calculated by equations 16 and 17.

Intakes from acidulation of CTO	**Mill B (no acidulation)**	**Mill A_1 (H_2SO_4 process)**	**Mill A_2 (Spent acid process)**	**Mill A3 ($CO2 + H_2SO_4$ process)**
$S_{acidulation}$ (kg/ADt)	0.00	2.68	9.03	1.34
$Na_{acidulation}$ (kg/ADt)	0.00	0.11	6.59	0.11

Based on the calculated intakes from acidulation presented in Table 6, the amount of sulfur and sodium addition or discharges was calculated. If the already known intakes are greater than discharges, fly ash is removed to balance the situation. Correspondingly, if discharges are greater than intakes, make-up chemicals are added.

The difference between inputs and outputs is calculated for sulfur as:

$$Difference_S\left[\frac{kg}{ADt}\right] = S_{wood} + S_{MgSO4} + S_{fuels} + S_{spent\ acid} + S_{acidulation} - S_{air} - S_{scrubber} - S_{fly\ ash,min} - S_{washing} - S_{CSS} - S_{CTO} - S_{turpentine}, \quad (19)$$

where

S_{wood} is the sulfur intake from wood, water and chemicals as kg/ADt (Table 3)

S_{MgSO4} is the sulfur intake from $MgSO_4$ from delignification as kg/ADt (Table 3)

S_{fuels} is the sulfur intake from fuels as kg/ADt (Table 3)

$S_{spent\ acid}$ is the sulfur intake from spent acid from ClO_2 plant as kg/ADt (Table 3)

$S_{acidulation}$ is the sulfur intake from acidulation of CTO as kg/ADt (Table 6)

S_{air} is the sulfur discharge to air emissions as kg/ADt (Table 3)

$S_{scrubber}$ is the sulfur discharge to scrubber salts as kg/ADt (Table 3)

$S_{fly\ ash,min}$ is the estimated minimum sulfur discharge with fly ash from electrostatic precipitors, 0.13 kg/ADt,

$S_{washing}$ is the sulfur discharge with washing losses to fiber line as kg/ADt (Table 3) and

S_{CSS} is the sulfur discharge with crude sulfate soap as kg/ADt (Table 3)

S_{CTO} is the sulfur discharge with crude tall oil as kg/ADt (Table 3) and

$S_{turpentine}$ is the sulfur discharge with turpentine as kg/ADt (Table 3).

If $Difference_S$ is smaller than zero, there are more discharges than intakes, and the situation needs to be balanced by adding sulfur in make-up chemicals. The need for sulfur is then:

$$S_{make\ up}\left[\frac{kg}{ADt}\right] = -Difference_S. \quad (20)$$

When there is deficit of sulfur, only the minimum amount is removed in fly ashes:

$$S_{fly\ ash}\left[\frac{kg}{ADt}\right] = S_{fly\ ash,min}. \quad (21)$$

If $Difference_S$ is zero, the intakes and discharges are balanced and there is no need for sulfur make-up or additional removal:

$$\mathrm{S_{make\ up}}\left[\frac{\mathrm{kg}}{\mathrm{ADt}}\right] = 0 \text{ and} \quad (22)$$

$$S_{fly\ ash}\left[\frac{kg}{ADt}\right] = S_{fly\ ash,min}. \quad (23)$$

Else, if $Difference_S$ is greater than zero, there is an excess of sulfur and no need for sulfur make-up chemicals. An additional amount of sulfur, equivalent of the $Difference_S$, is removed from the fly ash. The balanced make-up and fly ash amounts are then:

$$\mathrm{S_{make\ up}}\left[\frac{\mathrm{kg}}{\mathrm{ADt}}\right] = 0 \text{ and} \quad (24)$$

$$S_{fly\ ash}\left[\frac{kg}{ADt}\right] = S_{fly\ ash,min} + Difference_S. \quad (25)$$

Within the intake and discharge ranges specified in Table 2, the excess of sulfur is always greater than the excess of sodium, if there is excess at all. The fly ash is presumed to be Na_2SO_4, which means that there is always two moles of discharged sodium per one mole of discharged sulfur. The sodium discharge in fly ash is therefore defined by the greater sulfur removal need as:

$$Na_{fly\ ash}\left[\frac{kg}{ADt}\right] = 2 * \frac{M_{Na}}{M_S} * S_{fly\ ash}. \quad (26)$$

As the higher sulfur removal need inevitably results to removing more sodium than required for balancing the intakes and discharges, the excessively removed sodium needs to be replaced by adding sodium make-up chemicals. Now that the sodium removal in fly ash is known, the needed make-up amount can be calculated as the difference between intakes and discharges:

$$Na_{make\ up}\left[\frac{kg}{ADt}\right] = -(Na_{wood} + Na_{MgSO4} + Na_{fuels} + Na_{spent\ acid} + Na_{acidulation} - Na_{air} - Na_{scrubber} - Na_{fly\ ash} - Na_{washing} - Na_{CSS} - Na_{CTO} - Na_{turpentine}), \quad (27)$$

where all the variables for sodium are defined equally as for sulfur in kg/ADt, as listed in Table 3.

These calculations result to a balanced situation, were inputs and outputs are equal. The completed chemical balances of the reference mill B and mills with varying acidulation processes are presented in Table 7. The bolded values are the mill dependent calculated values for each mill, $S_{acidulation}$ and $Na_{acidulation}$ obtained from Table 6, $S_{make\text{-}up}$ obtained from equation 20 or 22, $Na_{make\text{-}up}$ from equation 27, $S_{fly\ ash}$ from equation 21 or 25 and $Na_{fly\ ash}$ from equation 26.

Table 7. Sodium and sulfur balances of the pulp mills studied. Mill dependent and calculated values are marked with bolded numbers. Intakes from acidulation are greatest from the spent acid process in mill A_2, causing also the greatest need for sulfur removal through fly ash in this mill. The sulfur intake from acidulation in mill A_3 is almost equivalent to the amount needed in order to balance the mill, which can be seen from the small amount of excess sulfur removal need through fly ash, where the minimum purge is set to 0.13 kg S/ADt.

		Reference mill B No acidulation		**Mill A_1 H_2SO_4 process**		**Mill A_2 Spent acid process**		**Mill A_3 $CO_2 + H_2SO_4$ process**	
		Sulfur	**Sodium**	**Sulfur**	**Sodium**	**Sulfur**	**Sodium**	**Sulfur**	**Sodium**
Intakes kg/ADt	Wood, water and chemicals	0.40	0.04	0.40	0.04	0.40	0.04	0.40	0.04
	MgSO4 from delignification	0.40	0.00	0.40	0.00	0.40	0.00	0.40	0.00
	Fuels	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	ClO_2 waste acid	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Acidulation of CTO	**0.00**	**0.00**	**2.68**	**0.11**	**9.03**	**6.59**	**1.34**	**0.11**
	pH adjustment /Make-up chemicals	**0.97**	**5.30**	**0.00**	**4.90**	**0.00**	**7.53**	**0.00**	**2.97**
	TOTAL	**1.77**	**5.34**	**3.48**	**5.05**	**9.83**	**14.15**	**2.14**	**3.12**
Discharges kg/ADt	Air emissions	0.19	0.00	0.19	0.00	0.19	0.00	0.19	0.00
	Scrubber salts	0.30	0.00	0.30	0.00	0.30	0.00	0.30	0.00
	Fly ash from electrostatic precipitators	**0.13**	**0.19**	**1.49**	**2.14**	**7.84**	**11.25**	**0.15**	**0.22**
	Washing losses to fibre line	0.90	2.90	0.90	2.90	0.90	2.90	0.90	2.90
	Crude sulfate soap	**0.20**	**2.25**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**
	Crude tall oil	**0.00**	**0.00**	**0.55**	**0.01**	**0.55**	**0.01**	**0.55**	**0.01**
	Turpentine	0.05	0.00	0.05	0.00	0.05	0.00	0.05	0.00
	TOTAL	**1.77**	**5.34**	**3.48**	**5.05**	**9.83**	**14.15**	**2.14**	**3.12**

As seen in the Table 7, mill B without acidulation has the only chemical balance that requires sulfur make-up (Na_2SO_4), as there is no intake of sulfur from acidulation. In pulp mills A_1 and A_2, with H_2SO_4 and spent acid processes, an excess of sulfur results to increased need for fly ash removal, which for mill A_2 is the highest, as the sulfur intake is highest. With the defined intake and discharge values, mill A_3 sulfur intakes and discharges are nearly balanced with the sulfur from acidulation, and the fly ash removal is only 0.02 kg S/ADt more than the minimum fly ash removal need. It should be noted, that in addition to acidulation intakes, difference between the A and B balances are created, as discharges of sulfur and sodium in CSS are larger than discharges in acidulated CTO.

In order to calculate the input and waste related emissions, the elemental additions of make-up chemicals and fly ash removal need to be converted to Na_2SO_4 and NaOH purchased and waste water generated.

First, the need for purchased Na_2SO_4 is determined by converting the sulfur make-up need to sodium sulfate in kg/ADt with equal molar amounts:

$$Na_2SO_{4,in,}\left[\frac{\text{kg}}{\text{ADt}}\right] = \frac{S_{make-up}}{\text{M}_\text{S}} * \text{M}_{\text{Na}_2\text{SO}_4}. \quad (28)$$

where

M_{Na2SO4} is the molecular weight of sodium sulfate, 142.04 g/mol.

Then, the amount is scaled per ton of CTO, as the final emission calculations are made for CTO. All the make-up chemical needs and wastewater amounts are scaled assuming equal CTO yield in all mills, in order to enable comparison, even though in the mill B without acidulation, no CTO is generated.

$$Na_2SO_{4,in}\left[\frac{\text{kg}}{\text{ton CTO}}\right] = \frac{Na_2SO_{4,in}\left[\frac{kg}{ADt}\right]}{\text{yield}_{\text{CTO}}} * 1000. \quad (29)$$

The need for purchased NaOH in kg/ADt is then calculated based on the sodium make-up need, subtracting the amount of sodium that was already obtained in Na_2SO_4 make-up:

$$NaOH_{in}\left[\frac{\text{kg}}{\text{ADt}}\right] = \frac{Na_{make-up} - \frac{Na_2SO_{4,in}}{M_{Na_2SO_4}} * \text{M}_{\text{Na}}}{\text{M}_{\text{Na}}} * \text{M}_{\text{NaOH}}. \quad (30)$$

Equally as for sulfur, the NaOH need is then scaled per ton of produced CTO:

$$NaOH_{in}\left[\frac{\text{kg}}{\text{ton CTO}}\right] = \frac{NaOH_{in}\left[\frac{\text{kg}}{\text{ADt}}\right]}{\text{yield}_{\text{CTO}}} * 1000. \quad (31)$$

The fly ash discharge in kg/ADt is calculated as Na_2SO_4 based on the sulfur amount in fly ash:

$$Fly\ ash_{out}\left[\frac{\text{kg}}{\text{ADt}}\right] = \frac{S_{fly\ ash}}{\text{M}_{\text{S}}} * \text{M}_{\text{Na}_2\text{SO}_4}. \quad (32)$$

The amount of fly ash is finally converted to wastewater per ton of CTO as

$$Waste\ water\left[\frac{\text{m}^3}{\text{ton CTO}}\right] = \frac{\left(\frac{Fly\ ash_{out}}{C_{\text{wastewater}}}\right)}{\text{yield}_{\text{CTO}}} * 1000, \quad (33)$$

where

$C_{\text{waste water}}$ is the estimated mass concentration of Na_2SO_4 in wastewater, 200 kg/m^3.

Table 8 summarizes the results of make-up chemicals needs and wastewater amounts for the cases studied. As seen already in Table 7, mill B has the only balance requiring sulfurous make-up Na_2SO_4. The NaOH make-up need is highest for the mill A_2 with spent acid process, as a large amount of sodium is removed in fly ash with excess sulfur. The wastewater generation is equally greatest in mill A_2 due to the large amount of fly ash removed. In mill A_3 with CO_2 pre-acidulation used, the make-up chemical need for sodium is lower than in mill B, as the inputs from acidulation balance the chemical cycle and the need for added removal of fly ash and therefore added sodium is very small. In the next section, these values are used for determining the emissions caused by the make-up need and fly ash removal in each case.

Table 8. Make-up Na_2SO_4 (equation 29) and NaOH (equation 31) need and wastewater (equation 33) generated due to fly ash discharge for reference mill without acidulation and mills integrated with three typical acidulation processes. To enable comparison, amounts are scaled per ton of CTO assuming equal yields of CTO in all mills, although no CTO is created in mill B.

	Mill B (No acidulation)	Mill A_1 (H_2SO_4 process)	Mill A_2 (Spent acid process)	Mill A3 (CO2 + H_2SO_4 process)	Unit
Na_2SO_4	107.35	0.00	0.00	0.00	kg /ton CTO
NaOH	170.25	212.98	327.37	129.38	kg /ton CTO
Waste water	0.07	0.83	4.34	0.08	m^3 /ton CTO

5.3.2 Emission calculations

Finally, the greenhouse gas emissions induced by acidulation were calculated based on the inputs of acidulation in Table 6 and pulp mill make-up, and wastewater amounts presented in Table 8. The conversion of the mass and volume streams to emissions was made by using emission factors listed in Table 5.

Equations 12 to 15 summarized the calculation method, where the emissions of the mill without acidulation (B) are subtracted from the emissions of the mill with acidulation (A). As the emission factors for electricity, steam and spent acid are zero, the equations are reduced to the following:

$$EM_{Ci}\left[\frac{kgCO_2eq}{ton\ CTO}\right] = \left(EM_{inputs,Ai} - EM_{inputs,B}\right) + \left(EM_{waste\ water,Ai} - EM_{waste\ water,B}\right)$$

$$= \left(H_2SO_{4_{Ai}} - H_2SO_{4_B}\right) * EF_{H_2SO_4} + \left(CO_{2_{Ai}} - CO_{2_B}\right) * EF_{CO_2} + \left(Process\ water_{Ai} - Process\ water_B\right) * EF_{Process\ water} + \left(NaOH_{Ai} - NaOH_B\right) * EF_{NaOH} + \left(Na_2SO_{4_{Ai}} - Na_2SO_{4_B}\right) * EF_{Na_2SO_4} + \left(waste\ water_{Ai} - waste\ water_B\right) * \mathrm{EF}_{\text{waste water}}. \quad (34)$$

As inputs in the acidulation plant for reference pulp mill B are zero, the same equation can also be written as

$$EM_{Ci}\left[\frac{\mathrm{kgCO_2eq}}{\mathrm{ton\ CTO}}\right] = \left[H_2SO_{4_{Ai,acidulation}} * EF_{H_2SO_4} + CO_{2_{Ai,acidulation}} * \mathrm{EF_{CO_2}} + Process\ water_{Ai,acidulation} * \mathrm{EF_{Process\ water}} + NaOH_{Ai,acidulation} * \mathrm{EF_{NaOH}}\right] + \left[\left(NaOH_{Ai,make-up} * \mathrm{EF_{NaOH}} + Na_2SO_{4_{Ai,make-up}} * \mathrm{EF_{Na_2SO_4}} + wastewater_{Ai,fly\ ash} * \mathrm{EF_{wastewater}}\right) - \left(NaOH_{B,make-up} * \mathrm{EF_{NaOH}} + Na_2SO_{4_{B,make-up}} * \mathrm{EF_{Na_2SO_4}} + wastewater_{B,fly\ ash} * \mathrm{EF_{wastewater}}\right)\right], \quad (35)$$

where the amounts of H_2SO_4, CO_2, process water and NaOH of acidulation are obtained from Table 4, amounts of NaOH and Na_2SO_4 make-up as well as wastewater from Table 8, and emission factors, EF_i, from Table 5.

The previous grouping of the variables equals to

$$EM_{Ci}\left[\frac{\mathrm{kgCO_2eq}}{\mathrm{ton\ CTO}}\right] = EM_{Ai,acidulation} + \left(EM_{make-up+waste,Ai} - EM_{make-up+waste,B}\right), \quad (36)$$

where $EM_{Ai,acidulation}$ is equal to the emissions of acidulation without considering the effects on chemical balance, as would be obtained in emission calculation using system boundary pictured in Figure 10.

For comparison, the results are divided in this manner in Table 7, where the *emissions of acidulation inputs* indicates the direct emissions caused by acidulation (system boundary of Figure 10). *Emissions induced in chemical cycle* take into account the indirect emissions caused or saved in the pulp mill due to acidulation-induced changes in the chemical balance of the mill. In Table 7, negative values in *emissions induced in the chemical cycle* for H_2SO_4 and CO_2+ H_2SO_4 processes indicate that less emissions are created in the pulp mill chemical recovery cycle with an acidulation process than in the mill B without acidulation, when the make-up need and fly ash discharge are considered. However, when the emissions induced in the chemical cycle are added together with the emissions of acidulation inputs, all processes result to have positive emission values, which means that with the estimated reference pulp mill values used, the emissions in total are higher in mills with acidulation (A) than in in a mill without acidulation (B).

Table 7. Total emissions of acidulation processes (EM_C), calculated as a sum of direct emissions from acidulation inputs and indirect emissions caused or saved in the pulp mill due to effects on the chemical balance. Negative emission values indicate, that less emissions are generated with acidulation than without acidulation.

		No acidulation (mill B)	**H_2SO_4 process (mill A_1)**	**Spent acid process (mill A_2)**	**CO_2 + H_2SO_4 process (mill A_3)**	**Unit**
Acidulation inputs	H_2SO_4	0.00	43.05	0.00	21.53	kgCO2eq/ton CTO
	Spent acid	0.00	0.00	0.00	0.00	kgCO2eq/ton CTO
	CO_2	0.00	0.00	0.00	136.31	kgCO2eq/ton CTO
	Process water	0.00	0.15	0.15	0.75	kgCO2eq/ton CTO
	NaOH	0.00	2.35	2.35	2.35	kgCO2eq/ton CTO
	Emissions of acidulation inputs ($EM_{Ai,acidulation}$)	**0.00**	**45.55**	**2.50**	**160.94**	kgCO2eq/ton CTO
Make-up and waste	NaOH	80.02	100.10	153.86	60.81	kgCO2eq/ton CTO
	Na_2SO_4	49.77	0.00	0.00	0.00	kgCO2eq/ton CTO
	Waste water	0.01	0.12	0.61	0.01	kgCO2eq/ton CTO
	SUM	**129.79**	**100.21**	**154.47**	**60.82**	kgCO2eq/ton CTO
	Emission induced in chemical cycle ($EM_{make-up+waste,Ai} - EM_{make-up+waste,B}$)		**-29.58**	**24.68**	**-68.98**	kgCO2eq/ton CTO
	TOTAL EMISSIONS OF ACIDULATION (EM_{Ci})		**15.97**	**27.18**	**91.96**	kgCO2eq/ton CTO

The results are visualized in Figure 11, where the relative amounts of acidulation input emissions ($EM_{Ai,acidulation}$), emissions generated by make-up chemical addition and emissions from wastewater treatment can be compared for all the processes. As seen, the effect of wastewater is negligible for all the processes. For spent acid process, the effect of acidulation input emissions are very small, but make-up chemical emissions are high. In contrary, CO_2 + $H2SO_4$ process results to the highest emissions from acidulation inputs due to the high emission factor of CO_2, but the emissions of make-up chemicals are the lowest of all processes compared. The baseline for zero emissions is set by the emissions of make-up chemicals and negligible wastewater of the reference mill B and the values above zero indicate the total emissions of acidulation process.

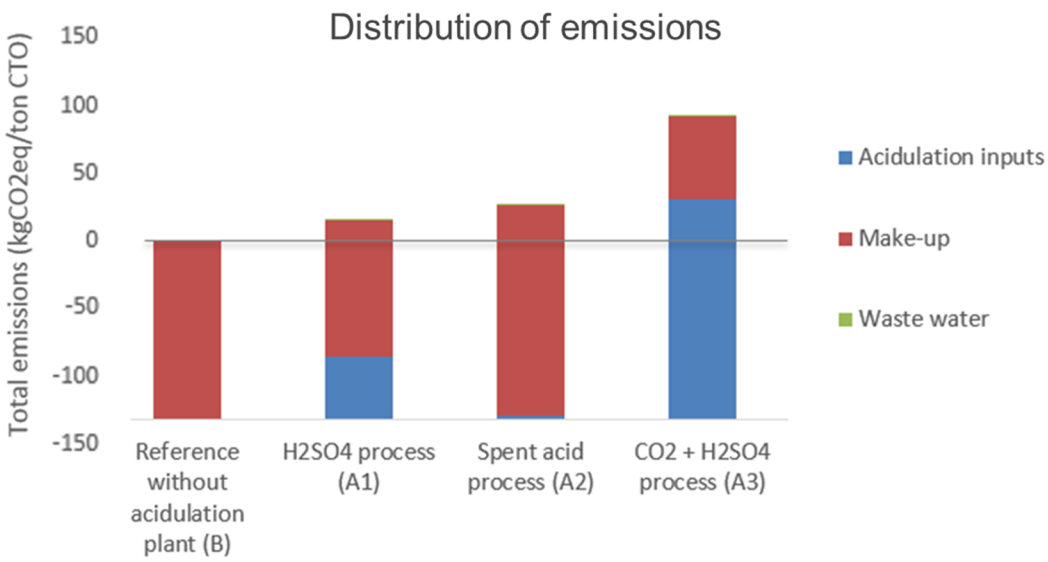

Figure 11. Distribution of emission between acidulation input emissions, make-up emissions and wastewater emission. Emissions of the reference mill B set the base line for total emission calculation. Make-up chemical need is accounted for most of the emissions in mills B, A_1 and A_2. High emissions of acidulation inputs correspond to the highest emissions of mill A_3. Wastewater caused emissions are negligible in all mills.

As seen in Table 7 and Figure 11, the emissions vary depending on the process and the influence of the emissions induced at the pulp mill, due to make-up additions, have a substantial effect on the total emissions of acidulation. Emissions calculated only based on the acidulation inputs (only blue blocks in Figure 11), as would be done with the system boundary set in Figure 10, do not provide a realistic view on the total emissions of acidulation process integrated with a kraft pulp mill. It must be noted, that the results presented are only valid for the reference pulp mill functioning as estimated in section 5.2.1 and using the defined, mostly 50% of range input and discharge values for sulfur and sodium. The emissions are re-calculated with varying input values in the sensitivity analysis of the next section and results are discussed in more detail in chapter 6.

5.4 Sensitivity analysis

It has already been noted, that both acidulation inputs and chemical balance of the pulp mill affect the total amount of acidulation emissions. A sensitivity analysis was performed in order to determine which input values have the largest effects on the total emissions of each process and to define how much effect the changes in each variable cause to the total emissions of acidulation. The analysis was made by repeating all the calculations by varying one input value at the time from its determined minimum value to its determined maximum value, while other variables were kept at the initial estimate, 50% of their range.

The input variables studied were chosen as the most important variables in both acidulation and chemical balance. These variables were the CTO yield, acid need in acidulation per ton of CTO and both sulfur and sodium intakes to and discharges from the chemical balance. Increasing CTO yield does not affect the acidulation input emission, as the use of inputs per ton of CTO is kept the same, but it increases the sulfur intakes to the chemical cycle. Growing acid need per ton of CTO on the other hand increases both the acidulation input emissions, except for spent acid process with zero emission factor, and sulfur intake to the chemical balance. The studied variables and corresponding ranges, based on information presented in chapter 3 and Table 2, are compiled to Table 8. Acid need in acidulation, as well as sulfur intakes and discharges and sodium discharges, are a combination of several input values that were changed at once with the same percentage of their range.

Table 8. Ranges studied in the sensitivity analysis. Lower limit is the minimum value, 0% of the range and the higher limit the maximum value, 100% of the range.

Variable	Values	Range	Unit	References
CTO yield	$yield_{CTO}$	30-50	kg/ADt	[27]
Acid need in acidulation	H_2SO_4 need in H_2SO_4 process	170-240	kg/ton CTO	[27, 28, 31]
	Spent acid need in spent acid process	800-1200	kg/ton CTO	estimated by [33]
	CO_2 need in CO_2 + H_2SO_4 process	139-196	kg/ton CTO	1.63 kg of CO_2 to replace 1 kg of H_2SO_4 [35]
	H_2SO_4 need in CO_2 + H_2SO_4 process	85-120	kg/ton CTO	50% of H_2SO_4 process use [28]
Sulfur intakes	S_{wood} intake from wood, water and chemicals	0.3-0.5	kg/ADt	[26, 34]
	S_{MgSO4} intake from $MgSO_4$ from delignification	0-0.8	kg/ADt	[26, 34]
Sulfur discharges	S_{air} sulfur discharge to air emissions	0.09-0.29	kg/ADt	[35, 41]
	$S_{scrubber}$ sulfur discharge to scrubber salts	0-0.6	kg/ADt	[34]
	$S_{washing}$ sulfur discharge to washing losses to fiber line	0.3-1.5	kg/ADt	[38]
	S_{CSS} sulfur discharge to crude sulfate soap (mill B)	0.1-0.3	kg/ADt	[36, 38]
	S_{CTO} sulfur discharge to crude tall oil (mills A_1, A_2, A_3)	0.1-1	kg/ADt	[27]
	$S_{turpentine}$ sulfur discharge to turpentine	0-0.1	kg/ADt	[36]
Sodium intakes	Na_{wood} sodium intake from wood, water and chemicals	0-0.07	kg/ADt	[27]
Sodium discharges	$Na_{washing}$ sodium discharge to washing losses to fiber line	1.3-4.5	kg/ADt	[38]
	Na_{CSS} sodium discharge to crude sulfate soap (mill B)	1.8-2.7	kg/ADt	[36, 38]
	Na_{CTO} sodium discharge to crude tall oil (mills A_1, A_2, A_3)	0-0.01	kg/ADt	[27, 36]

The results of the sensitivity analysis are compiled to the following figures, where the total emissions of acidulation are plotted against the percent of range of variables studied. 0% equals the minimum, and 100% the maximum of the range of each variable. The changes in the total emissions are pictured in Figure 12 for the H_2SO_4 process, in Figure 13 for the spent acid process and in Figure 14 for the CO_2 + H_2SO_4 process.

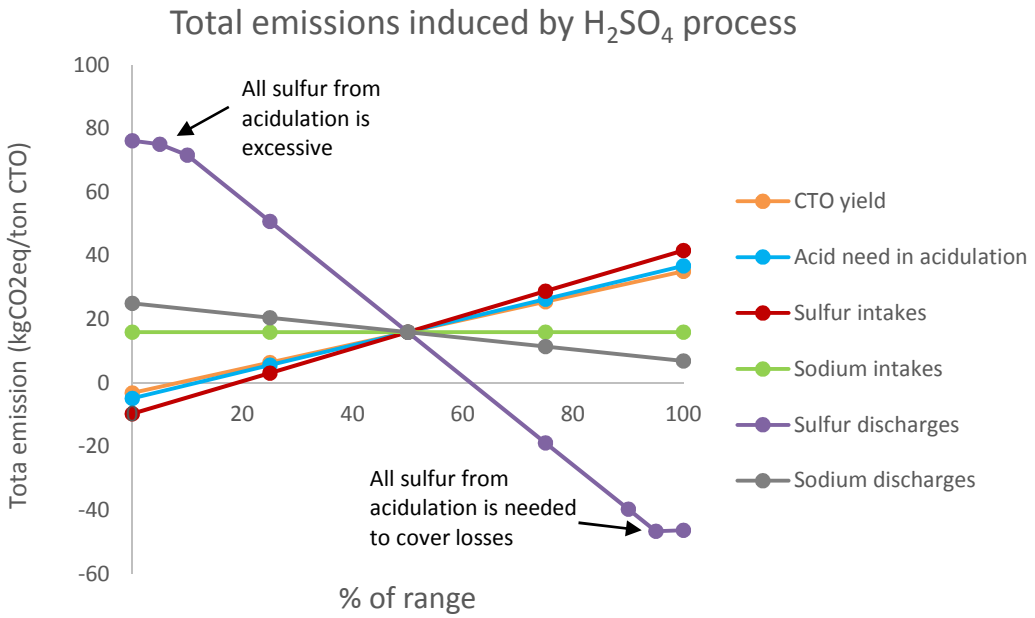

Figure 12. Total emissions of H_2SO_4 acidulation with varying input values. Each variable is altered from 0%, which is the minimum, to 100%, which is the maximum of the range specified in Table 10, while other variables are kept constant. Non-linearity of the total emissions (C) is explained as the emissions of a mill with acidulation (A) and emissions of mill (B) are changing at different rates.

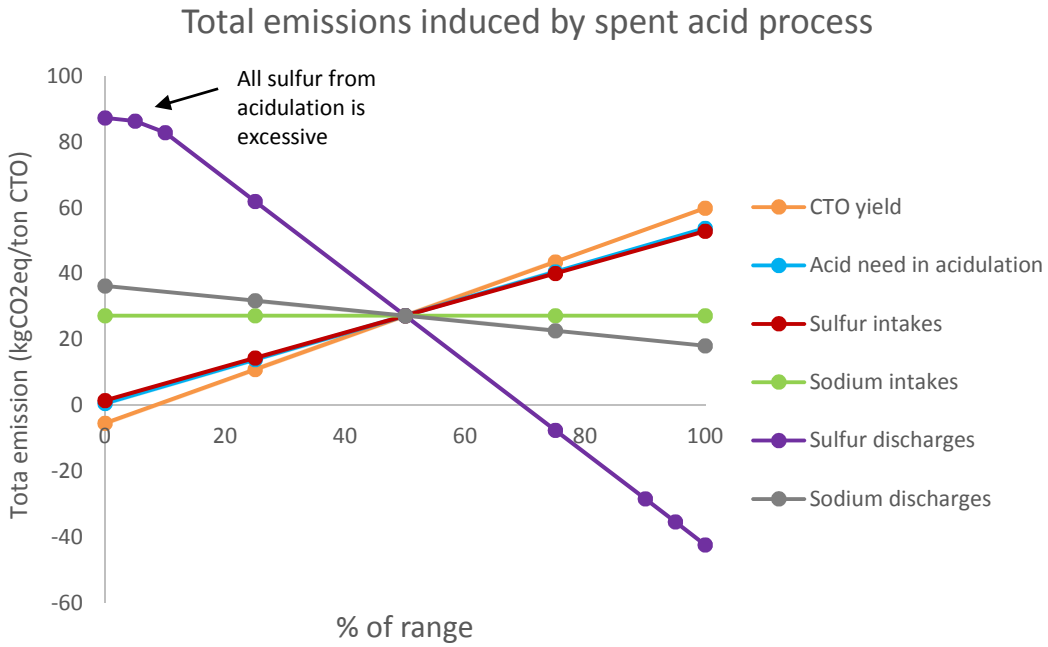

Figure 13. Total emissions of spent acid acidulation with varying input values. Each variable is altered from 0%, which is the minimum, to 100%, which is the maximum of the range specified in Table 10, while other variables are kept constant. Non-linearity of the total emissions (C) is explained as the emissions of a mill with acidulation (A) and emissions of mill (B) are changing at different rates.

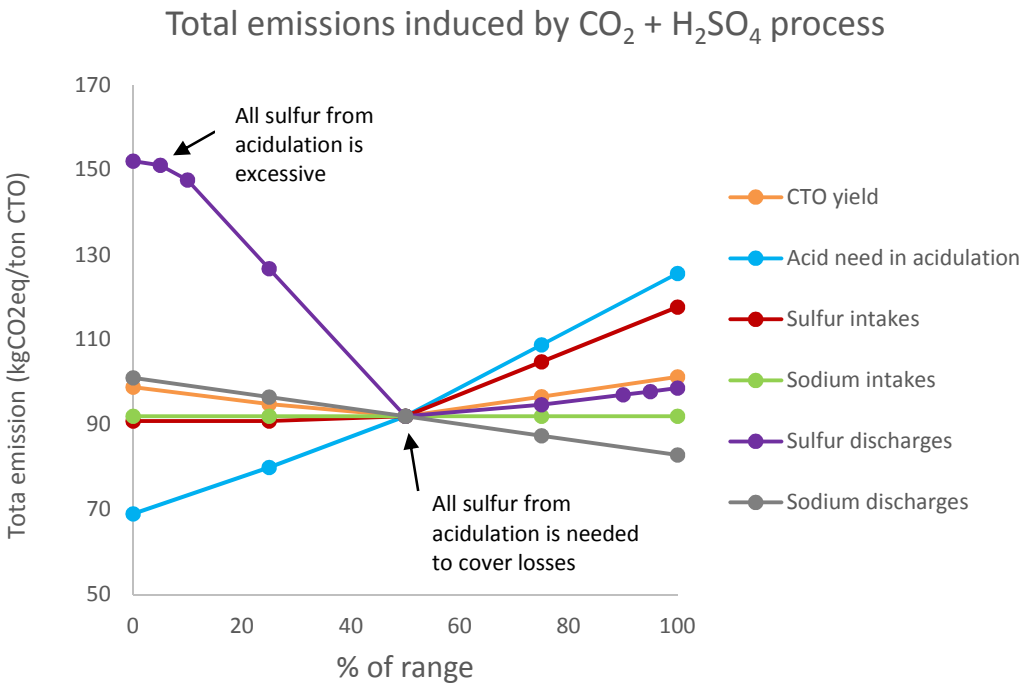

Figure 14. Total emissions of CO_2+ H_2SO_4 acidulation with varying input values. Each variable is altered from 0%, which is the minimum, to 100%, which is the maximum of the range specified in Table 10, while other variables are kept constant. Non-linearity of the total emissions (C) is explained as the emissions of a mill with acidulation (A) and emissions of mill (B) are changing at different rates.

As seen in the figures 12, 13 and 14, all process types are most sensitive to the changes in the sulfur discharges of the pulp mill within the specified ranges. Depending on the sulfur balance, the total emissions can be either positive or negative for the H_2SO_4 and spent acid processes. The highest emissions are related to CO_2 pre-acidulation process, where the total emissions are positive independent of the sulfur balance of the pulp mill. This is due to the high emissions of acidulation inputs, due to the use of emission intensive purchased CO_2. The acidulation input emissions are independent of the chemical balance.

In general, the total emissions are increased when the sulfur amount in the chemical cycle is increased by moving to higher percent of range in CTO yield, acid need in acidulation, and sulfur intakes. Vice versa, the total emissions are generally decreased by moving to higher percent of range in sulfur discharges and sodium discharges. The sodium intakes have no effect on the total emissions, as the range for the inputs is very narrow. The general observations however, are only partially true for the CO_2 + H_2SO_4 process. Nonlinearity of the emissions is observed for all the processes, when moving to small

sulfur discharges, and again with higher sulfur discharges for H_2SO_4 CO_2 + H_2SO_4 process. The points, where the emission change rate changes, are points where either all the sulfur from acidulation becomes excessive in the chemical balance or all the sulfur from acidulation becomes needed to cover the sulfur losses of the balance.

In more detail, the changing differential coefficient of the emissions relates to several reasons. First, the total emissions reach a local minimum value when the sulfur discharges are sufficiently high. This is seen in Figure 12 at 95% of range and in Figure 14 at 50% of range. This minimum-emission situation is equal to the point where both fly ash discharge need and make-up chemical need in the pulp mill with acidulation are minimized. The exact amount of sulfur input from acidulation is therefore needed for the chemical balance without excess. Without this acidulation intake in mill B, corresponding amounts of sulfur are needed as make-up chemicals. When the sulfur discharges increase towards this point, the emissions are decreased, as the excess of sulfur is decreased. This leads to decreasing need for fly ash removal, and correspondingly to smaller amount of sodium make-up, which results to smaller make-up chemical emissions in mill A. In contrary, when the sulfur discharges increase further from this point, Na_2SO_4 make-up is needed in mill A in addition to the sulfur intake from acidulation, and total emissions start to increase due to the emissions caused by this added make-up need. As the sulfur addition in H_2SO_4 process in larger than in the CO_2 + H_2SO_4 process, the minimum emissions are reached with a higher sulfur discharge level than for CO_2 + H_2SO_4 process. The sulfur addition to the chemical cycle from spent acid process is so high, that the amount of sulfur is always excessive within the ranges studied.

In addition to sulfur discharges, a similar local emission minimum is observed in Figure 14, for CTO yield. The reason for this minimum is the same that for sulfur discharge, just vice versa, as increasing CTO yield results to increasing acid consumption and sulfur addition to chemical cycle. Equally as for sulfur discharge, in the minimum emission point, the sulfur from acidulation covers the balance sulfur need without addition of sulfurous make-up or need for discharging excess sulfur through fly ash.

Near the minimum sulfur discharge, the change in the emissions is very slow. When the discharges are increased from 0% of range, both A and B mills have an excess of sulfur,

and there is a decreasing need for additional sulfur removal from fly ash with increasing sulfur discharges. This results to decreasing sodium make-up need in both A and B mills. However, the sodium make-up need in mill A decreases faster than that for mill B, and the total emission (EM_A-EM_B) are slowly decreased with increasing sulfur discharge from 0% of range. In 0-6% of sulfur discharge range, more than the sulfur from acidulation is excessive in all A mills. From 6% of range onwards, some of the sulfur intake from acidulation in A mills is needed to cover the losses in chemical recovery cycle. Due to higher discharges of sulfur in CSS than CTO, mill B reaches its balance at 8% of the sulfur discharge range and from 8% onwards, sulfur make-up (Na_2SO_4) is needed at the B mill. Hence, from 8% of sulfur discharge range, until all sulfur from acidulation becomes needed to cover the sulfur losses, the change in emissions (EM_A-EM_B) is fast as EM_A decreases and EM_B increases.

In summary, the sulfur balance of the pulp mill is the most significant variable in the total emission calculations of acidulation processes. The sulfur balance is affected by the CTO yield, acid need in acidulation and other sulfur intakes and discharges, but considering the ranges, the sulfur discharges have the greatest effect on the total emissions of acidulation. The emissions of acidulation inputs on CO_2 + H_2SO_4 process are higher than for other processes, due to high emission factor of purchased CO_2, and therefore they are less sensitive to the sulfur balance changes. If the CO_2 used in acidulation could be collected from inside the pulp mill as a waste, the total emissions of CO_2 + H_2SO_4 process would be much lower, at 50% of sulfur discharge range below zero. Total emissions of H_2SO_4 and spent acid process can obtain either positive or negative values, depending on the pulp mill sulfur balance. The negative total emission values indicate that from the emission point of view, it is better to balance the pulp mill sulfur deficit by sulfur from acidulation, than by separate make-up chemicals.

As seen in the sensitivity analysis, changing the initial values through the ranges of the variables changes the results in a large scale. Therefore, it is impossible to estimate a typical emission value for an acidulation process, as each pulp mill has a different chemical balance and is optimized differently considering all the interlinked processes together. Most uncertainty in the initial estimates was related to the chemical balance of the pulp mill. However, results are comparable with a study by Ehtonen *et al.* [31], where using

different pulp mill balances, it was similarly to this work concluded, that substituting half of the H_2SO_4 by CO_2 in acidulation, results to balanced sulfur situation without the removal need for excess sulfur. In this work, the same conclusion is seen as the local minimum emission point in Figure 14.

If spent acid from ClO_2 plant would be directed to the chemical recovery cycle, contrary to the presumption made in this work, the sulfur intake of the balance would be higher. This would lead to higher emissions for all acidulation processes, as most sulfur from the acidulation would be excessive in the balance. However, in modern mills with high sulfidity, the spent acid is preferably used elsewhere than in the chemical recovery cycle. The estimated acidulation input amounts were probably realistic for most mills, as these variables are less affected by the set-up of the whole mill integrate. Tall oil yied could in some cases vary more than in the range specified in this work. In this case, the yield of tall oil would have a larger effect on the process emissions of acidulation, but that would not make the effect of sulfur balance any less significant.

However, the conclusion, that the pulp mill sulfur balance affects the emissions of acidulation in an integrated kraft mill, is independent on the initial presumptions made. The results presented are in line with the earlier conclusion, that the pulp mill chemical balance cannot be separated from the calculation of acidulation emissions and hence emissions of acidulation cannot be separated from emissions of the pulp mill. This result is generalizable in Northern coniferous forest belt, in North America and North Europe and Asia, where acidulation processes are interlinked with kraft pulping.

6 Discussion and recommendations

The total emissions of acidulation are studied in this work, as the residue status of CTO has been questioned especially due to this processing step in the kraft pulp mill. The current EU policy does not provide clear instructions on neither defining wastes and residues nor calculating raw material processing emissions. The instructions provided in RED Annex V Part C on calculating processing emissions, are all aimed for the processing of the final biofuel. [1] However, as no other instructions are given, it must be assumed that the same rules apply also for raw material processing.

Crude sulfate soap, from which CTO is generated in acidulation, is undoubtedly a processing residue from pulp production, as it separates unavoidably and has to be removed from the pulping process to optimize pulp production [26, 25]. Without further knowledge, it would seem appealing to classify CSS a residue, and add acidulation emissions to the lifecycle analysis of a CTO based biofuel. However, as the acidulation process in interlinked with the pulping process, this approach has two major drawbacks.

First, the configuration of the acidulation process in a pulp mill, presented in Figure 15, is directly comparable to the concept of a refinery, defined by the certification schemes [21, 22], and pictured in Figure 2. According to this definition of a refinery, processing emissions should be determined for the whole pulp mill, and then divided between the products, allocating zero emissions to wastes and residues [1]. In this approach, considering CSS a residue from pulp production would be equal to allocating zero emissions to an intermediate stream inside the system boundary, which is clearly against the allocation rule [1]. This refinery rule is most probably set, because the division of emissions from different process parts is extremely difficult, as concluded in this work.

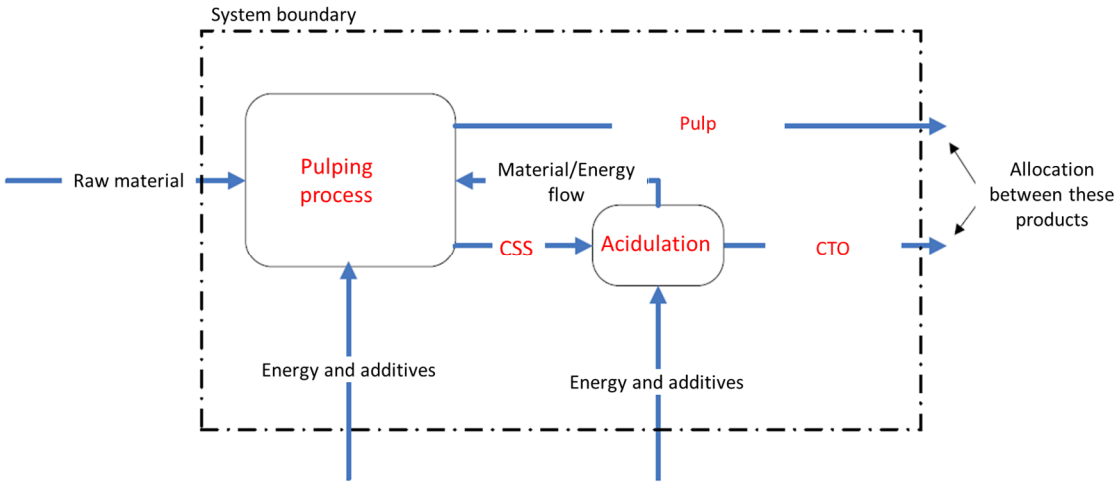

Figure 15. Allocation of emissions should happen between CTO and pulp, if original rule presented in Figure 2 was followed. Allocating zero emissions to CSS is not possible as the pulping process and acidulation form an interlinked process.

Second, a refinery, in this case a pulp mill, is optimized as a unity, in this case for pulp production. Changes in material balances affect the pulp mill processes as a whole. Therefore, forcing the system boundary of emission analysis only around specific process equipment does not provide realistic information of the emissions on the unit operation level. Moreover, even if the emissions of a certain process part could in theory be calculated separately, like in this work, there are multiple variables affecting the result that are optimized according to the total optimal control of the refinery. In this case, these variables affecting the emissions of acidulation are related to the sulfur balance of the mill.

As concluded in the sensitivity analysis in section 5.4, the emissions of acidulation are mostly dependent on the sulfur balance of the pulp mill, which is optimized for pulp production. Hence, the emissions of producing CTO cannot be separated from the emissions of producing of pulp. Depending on the pulp mill sulfur balance and acidulation process used, the calculated emissions of acidulation vary from -47 kgCO2eq /ton of CTO to 152 kgCO_2eq /ton of CTO. Negative emissions values indicate that the total emissions of the pulp mill are in certain cases reduced by the addition of acidulation process to the pulp mill, as considering the emissions, acidulation is a better way to provide sulfur to the chemical balance, than direct make-up chemical additions.

The highest emission levels of the acidulation processes studied are related to the CO_2 + H_2SO_4 acidulation process, where the total emissions of acidulation are always above zero. However, the decision for implementing a CO_2 pre-acidulation process instead of using only H_2SO_4, which would have lower emissions, is made in order to control the sulfur balance of the pulp mill by restricting sulfur intake in mother liquid. Therefore, the emissions of acidulation process are always dependent on the control of the pulp mill sulfur balance, which is optimized for pulp production, not CTO production. As the optimization of pulp production affects the acidulation emissions the most, these emissions should be allocated to pulp, rather than to CTO.

The results of this work support the use of the refinery rule [1] also for processing of biofuel feedstocks, as reliable separation of the emissions of interlinked processes is not possible. As CSS is clearly a residual stream from pulping and no emissions can be allocated to CTO from acidulation, it is recommended that CTO is regarded a residue from pulp production in EU biofuel legislation.

Another aspect supporting this conclusion is that acidulation is a predetermined processing step in the total pulp mill optimization. CSS is inevitably separated from pulp production and acidulation is an optimal way to dispose it and recycle the valuable cooking chemicals. A predetermined normal processing step does not prevent a material to be considered a residue. For example, RED lists crude glycerine as a processing residue although like CTO, it is generated in an additional process. Crude glycerine is a side-stream from conventional biodiesel (FAME) processing after separation of glycerine containing stream from FAME containing phase, it is often neutralized by an acid, and water and alcohol are removed from the crude glycerine by distillation [45]. As the resulting pre-treated crude glycerine stream is considered a residue by the European Union, it would be inconsistent not to regard CTO as one.

7 Conclusions

In this work, a method for calculating the process emissions of CSS acidulation to CTO was created and implemented for three common acidulation processes. Conclusions were made on whether these emissions can be separated from the emissions caused by the pulp production in a kraft mill and recommendations on the classification of CTO in EU biofuel policy were provided according to results.

The acidulation process is directly interlinked with the kraft pulp mill and constitutes a major intake of sulfur to the chemical recovery cycle of the mill. The method created in this work for the calculation of acidulation emissions, takes into account the effects of acidulation on the chemical recovery cycle of the mill. In the calculation method, the total emissions of acidulation were determined by the difference between the emissions of a pulp mill with an acidulation process and the emissions of an identical pulp mill without an acidulation process. This approach was built in line with the directions set in the Renewable Energy Directive, which specifies that the emissions of a refinery, build of several interlinked processes, shall be analyzed on the refinery level. The method was used for calculating the process emissions of acidulation by sulfuric acid, acidulation by spent acid and acidulation by carbon dioxide and sulfuric acid. The sensitivity of the emissions to different variables, from their minimum to the maximum value, was analyzed, as most of the variables were determined as typical ranges, rather than typical values.

It was observed, that depending on the acidulation process and the sulfur balance of the pulp mill, acidulation could either increase or decrease the emissions of the whole pulp mill in comparison to the mill without acidulation. The total emissions of all studied acidulation processes were found to be the most sensitive to discharges of sulfur from the pulp mill chemical balance. No typical value for the emissions of any of the processes could be assigned, due to the strong dependence of the emissions on the sulfur balance, which varies by mill and time, and is controlled for optimization of pulp production. As acidulation emissions depend more on pulp production than on CTO production, the emissions of pulp processing and CTO processing in acidulation cannot be separated and allocated to CTO.

In conclusion, CSS is clearly a residual stream, but according to the Renewable Energy Directive, no allocation of zero emissions should be done to CSS as it is an intermediate stream. In addition, the emissions of converting CSS to CTO in acidulation cannot be separated from the emissions of pulp processing. Therefore, no processing emissions can be allocated to CTO and it is recommended that CTO is considered a residue of pulp production in the EU legislation.

References

1. Directive 2009/28/EC of the European parliament and of the council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC, OJ L 140, April 23, 2009, p.16-62.

2. Tuovinen, J., Arizona Chemicals, Statement regarding the Finnish Ministry on Employment and the Economy's documentary TEM/2930/03.01.01/2011, 2011.

3. Real green gold web page, Arizona Chemical, Forchem, Respol, http://www.realgreengold.com/what-is-at-stake/. Accessed: May 28, 2015.

4. Directive 2009/30/EC of the European Parliament and of the Council of 23 April 2009 amending Directive 98/70/EC as regards the specification of petrol, diesel and gas-oil and introducing a mechanism to monitor and reduce greenhouse gas emissions and amending Council Directive 1999/32/EC as regards the specification of fuel used by inland waterway vessels and repealing Directive 93/12/EEC, 2009/30/EC, OJ L 140, p. 88-113.

5. Laki biopolttoaineista ja bionesteistä 393/2013 (Act on biofuels and bioliquids), 393/2013, June 7, 2013.

6. Laki biopolttoaineiden käytön edistämisestä liikenteessä 446/2007 (Distribution obligation act), 446/2007, December 30, 2010.

7. Communication from the Commission on the practical implementation of the EU biofuels and bioliquids sustainability scheme and on counting rules for biofuels, 2010/C 160/02, OJ C 160, p. 8-16.

8. Finnish Energy Authority web page: Approved sustainability management systems, http://www.energiavirasto.fi/hyvaksytyt-kestavyysjarjestelmat. Accessed: May 28, 2015.

9. New GHG requirements for Voluntary Sustainability Schemes, Biofuels International, http://biofuelsnews.com/display_news/8673/new_ghg_requirements_for_voluntary_sustainability_schemes/. Accessed: January 28, 2015.

10. Ecofys, Observations on advanced biofuel feedstocks and policies in the EU, Unpublished report, 2014.

11. ePure, Overview of the biofuel policies in EU-28 Member States, Unpublished report, 2014.

12. Position of the European Parliament adopted at second reading on 28 April 2015 with a view to the adoption of Directive (EU) 2015/... of the European Parliament and of the Council amending Directive 98/70/EC relating to the quality of petrol and diesel fuels and amending Directive 2009/28/EC on the promotion of the use of energy from renewable sources, P8_TA(2015)0100, April 28, 2015.

13. ISCC System GmbH , Lists of material eligible for ISCC EU certification, November 24, 2014.

14. Federal Office for Agriculture and Food of Germany, List regarding the concretion of possible materials which can be credited as waste and residues for the GHG-quote pursuant to § 37 a para. 4 of the BImSchG, 2015.

15. Regeling van de Staatssecretaris van Infrastructuur en Milieu, van 27 november 2014, nr. IenM/BSK-2014/259021, houdende vaststelling van regels ter uitvoering van titel 9.7 Hernieuwbare energie vervoer van de Wet milieubeheer en van het Besluit hernieuwbare energie vervoer 2015 (Act on renewable energy in transport 2015), IenM/BSK-2014/259021, November 27, 2014.

16. Swedish Energy Agency , Vägledning till regelverket om hållbarhetskriterier för biodrivmedel och flytande biobränslen (Guidance on the regulatory framework of sustainability criteria for biofuels and bioliquids), 2012.

17. UK Government, Renewable Transport Fuel Obligation (RTFO) Guidance: List of Wastes and Residues year 7 version 7.3, 2015.

18. Panda, D.H. , *Handbook on Tall Oil Rosin Production, Processing and Utilization*, Asia Pacific Business Press Inc., Delhi 2013, 480 p.

19. Communication from the Commission on voluntary schemes and default values in the EU biofuels and bioliquids sustainability scheme, 2010/C 160/01, OJ C 160, June 19, 2010, p. 1-7.

20. European Commission web page: Voluntary schemes, http://ec.europa.eu/energy/en/topics/renewable-energy/biofuels/voluntary-schemes. Accessed: January 28, 2015.

21. ISCC System GmbH, ISCC 205 GHG Emissions Calculation Methodology and GHG Audit v. 2.3 EU, 2011.

22. Finnish Energy Authority, Lain biopolttoaineista ja bionesteistä mukainen Toiminnanharjoittajan kestävyyskriteeriohje (Sustainability criteria instructions for operators according to Act on biofuels and bioliquids), 2013.

23. The ecoinvent Database version 2.2, Ecoinvent, http://www.ecoinvent.org/database/database.html.

24. Biograce GHG calculation tool 2011, Biograce, http://www.biograce.net/content/ghgcalculationtools/recognisedtool/.

25. KnowPulp 10.0, AEL, http://know.aalto.fi.libproxy.aalto.fi/pulp/latest/english/kps/ui/frontpage.htm. Accessed: March 18, 2015.

26. European IPPC Bureau, Best Available Techniques (BAT) Reference Document for the Production of Pulp, Paper and Board, FINAL DRAFT, 2013.

27. UPM Biorefining, Internal documentation, 2015.

28. Pikka O., *Sulfaattisellutehtaan rikki- ja natriumtase*, Licenciate thesis, Helsinki University of Technology, Laboratory of Pulping Technology, Espoo 1979, 162 p.

29. Vuorikari O., Tanner T., Koistinen J., Sarkkinen K. and Mattelmäki E., Method for acidification of soap with sodium bisulphite solution, CA2148232 C, 2000.

30. Maunus-Tiihonen M., Suovan käsittely ja mäntyöljyn valmistus, UPM internal report, 2006.

31. Ehtonen P., *Methods to balance the kraft pulp mill*, Doctoral thesis, Helsinki University of Technology, Department of Chemical Technology, Espoo 1997, 95 p.

32. Morris C. and Watkins G., Tall oil recovery, US 3575952 A, 1971.

33. Canifru J., Process for obtainiing tall oil from a sodium sesquisulfate solution, US20130172527 A1, 2013.

34. Pöyry SmartTerminal online service, Pöyry Management Consulting, https://www.jpsmartterminal.com/clients/. Accessed: January 28, 2015.

35. Ehtonen P., Hurme M. and Järveläinen M., *Integrated Chemical Plants at the Pulp Mill*, Helsinki University of Technology, Laboratory of Chemical Engineering, Plant Design Report Series 37, Espoo 1995, 24 p.

36. Kontu T., *Sodium and sulfur balances of a kraft pulp mill*, Master´s thesis, Aalto University, Department of Forest products Technology, Espoo 2010, 91 p.

37. Commission Implementing Decision of 26 September 2014 establishing the best available techniques (BAT) conclusions, under Directive 2010/75/EU of the European Parliament and of the Council, for the production of pulp, paper and board, OJ L 284, September 26, 2014, p. 76-125.

38. Keitaanniemi O., *Eräiden alkuaineiden määrät ja käyttäytyminen sulfaattisellutehtaan kierroissa*, Helsinki University of Technology, Department of Forest Product Technologies, Laboratory of Chemical Pulping, Espoo 1977, 117 p.

39. Ali M. and Sreekrishnan T., Aquatic toxicity from pulp and paper mill effluents: a review, *Adv. Environ. Res.* **5** (2) (2001) 175-196.

40. AkzoNobel web page: Chlorine dioxide technology, https://www.akzonobel.com/eka/products/plant_equipment_it/eka_engineering/products_services/chlorine_dioxide_tech/. Accessed: January 14, 2015.

41. Environmental Impact Assessment of Äänekoski Bioproduct mill, Metsä Fibre. The Centre for Economic Development, Transport and the Environment of Central Finland, 2014.

42. Valmet web page: Ash leaching and crystallization solutions, http://www.valmet.com/Valmet/products/Vault2MP.nsf/BYWID/WID-130603-2256E-8AC31/$File/HPGB_B_2300_018-02.pdf?OpenElement. Accessed: May 28, 2015.

43. Nurmesniemi H., Pöykiö R. and Keiski R.L., A case study of waste management at the Northern Finnish pulp and paper mill complex of Stora Enso Veitsiluoto Mills, *Waste manage*. **27** (2007) 1939-1948.

44. Ehtonen P., Golam S. and Hurme M., Studies on the ecologically balanced ECF pulp mill, *International pulp bleaching conference*, Halifax 2000, p. 205-208.

45. Leung D., Wu X. and Leung M., A review on biodiesel production using catalyzed transesterification, *Appl. Energy* **87** (2010) 1083-1095.